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PRELIMINARY PROBLEM DEFINITION STUDY OF  
48 MUNITIONS-RELATED CHEMICALS

VOLUME II PROPELLANT RELATED CHEMICALS

FINAL REPORT

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April 1978

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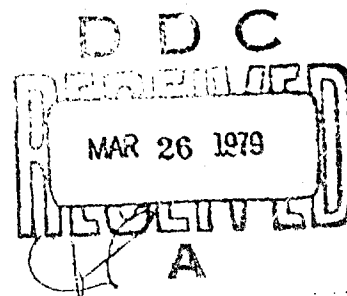
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Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

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ATLANTIC RESEARCH CORPORATION  
Alexandria, Virginia 22314

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Results are presented of a preliminary problem definition study on propellant related chemicals. The purpose of this study was to determine the Army's responsibility for conducting further research on these chemicals to determine toxicological and environmental hazards, so that effluent stan- dards can be recommended. Both civilian and military uses of the chemical were evaluated.		

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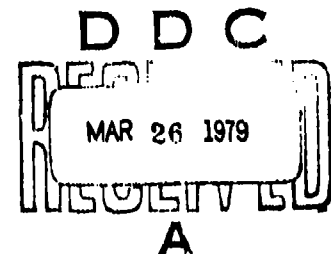
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## EXECUTIVE SUMMARY

The goal of the preliminary problem of definition study on propellant-related compounds was to assess the Army's responsibility for conducting additional toxicological and environmental evaluations on these compounds. The specific propellant-related compounds evaluated during this program were

- ethyl centralite
- diphenylamine
- diethyleneglycol dinitrate
- 2-nitrodiphenylamine
- N-nitrosodiphenylamine
- the phthalate esters (diethyl,-dibutyl-and diethylhexyl-)
- triacetin
- lead salicylate
- lead stearate
- ~~lead resorcyate~~

In order to assess the Army's responsibility for conducting further studies on these compounds, the civilian and military production, usage and pollution of each compound were comparatively evaluated. A preliminary overview of the toxicological and environment hazards was also made. The recommendations for each compound are summarized in Table S-1. The results and recommendations are summarized below.

### Ethyl Centralite

Ethyl centralite is a stabilizer used in solid propellant formulations in percentages from 0.02 to 6.5%. Current consumption of the chemical at Radford AAP is 372,000 lb/year. Discharges of ethyl centralite into the New River are estimated at 300 to 530 lb/month at current operation levels. At full mobilization, 1.8 million lb/year would be used by Radford AAP alone. Discharges up to 2500 lb/month could occur.

At the present time there are no producers of ethyl centralite in the United States. There is one manufacturing facility for ethyl centralite in the United States, however; it is currently not operational. The supplies of ethyl centralite are obtained from French or German sources.

Only one mammalian toxicity study on ethyl centralite was uncovered during this preliminary overview. These researchers found an intraperitoneal LD50 of 200 mg/kg for mice. In an aquatic toxicity study with salmon, ethyl centralite was shown to be extremely toxic to aquatic life.

Thus, ethyl centralite is a compound that is unique to propellant manufacturing. Since the military is one of the main formulators of propellants, ethyl centralite can be considered a military unique chemical. Therefore, it is recommended that the Army initiate the following studies to further evaluate the toxicological and environmental hazards of ethyl centralite:



# Recommendations for Phase II

Compound	Toxicological Evaluations		Environmental Evaluations		Additional Recommendations	
	Yes	No	Yes	No	Analysis of sediment and biota samples from RAAP	Sampling and analysis of effluent streams at RAAP
Ethyl Centralite						
Diphenylamine	No		Yes			
Diethyleneglycol Dinitrate	No		No			
2-Nitrodiphenylamine	Yes		Yes			
N-Nitrosodiphenylamine	No		No			
Diethyl Phthalate	No		No			
Dibutyl Phthalate	No		?			
Diethylhexyl Phthalate	No		No			
Triacetin	No		?			
Lead Salicylate	Yes		Yes		Sampling and analysis of effluent, sediment and biota at RAAP	
Lead Stearate	No		No			
Lead Resorcyate	Yes		Yes		Determination of physical and chemical properties. Sampling and analysis of effluent, sediment and biota at RAAP	

- a Phase II detailed literature evaluation
- analysis of sediment and biota samples from Radford AAP
- aquatic toxicity studies if the literature evaluation reveals the need for more information

### Diphenylamine

Diphenylamine is used in single base solid propellant formulations produced by the solvent process at Radford, Sunflower, Badger and Indiana Army Ammunition Plants (AAP). It is present in the propellants in amounts ranging from 0.5 to 1.7%. Current use of diphenylamine at Radford AAP is 120,000 lb/year. At full mobilization, 1,284,000 lb/year of diphenylamine would be formulated into propellants at Radford AAP. Estimated discharges of diphenylamine into the New River are between 1600 and 2650 lb/month at full mobilization. If all four propellant plants were utilizing this chemical at approximately the same full mobilization rate, the Army would need 5,136 million lb of diphenylamine per year.

Diphenylamine is used in the civilian community as an intermediate for a variety of dyes and as an antioxidant for rubber. In 1974 civilian production of this compound was 39.9 million lb/year. This production rate will increase as the dye and rubber market grows and as planned new diphenylamine production facilities become operational.

Diphenylamine is moderately toxic to mammals in acute doses. The major problem of chronic exposure to this chemical is the presence of 4-amino-biphenyl as an impurity. The presence of this carcinogen has overshadowed some of the results of chronic exposure studies with diphenylamine.

Diphenylamine is highly toxic to aquatic organisms with 48 hour LC50 ranging from 0.35 to 3.2 ppm. Microorganisms are able to produce nitrosamine from nitrate and diphenylamine. These compounds can be further degraded. However, their effect on the environment has not been resolved.

Diphenylamine is not a military unique chemical. The current Army use rate of this chemical is only 0.02% of the 1974 civilian production. At full mobilization, the Army's needs could increase to 13% of the 1974 production. Sufficient information is not available to assess the civilian pollution of this chemical. The pollution of this chemical resulting from current propellant manufacture at Radford AAP is estimated at 1800 to 3000 lb/year. This discharge is probably ~5% of that from civilian production and use. Therefore, the Army's responsibility for further research on this chemical is questionable. However, due to the high aquatic toxicity of diphenylamine, very low levels (12ppb) have been suggested for protection of aquatic organisms. If this suggested level is adopted, the Army may not be able to meet the effluent standard. Therefore, it is recommended that the following studies be undertaken

- Sampling and analysis at Radford be performed to determine the quantity of the compound entering the New River

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- A literature evaluation of the fate of this chemical in the ecosystem and in proposed treatment facilities
- Depending on the results of the literature evaluation, experimental studies on the fate of this compound may be necessary.

#### Diethyleneglycol Dinitrate

Diethyleneglycol dinitrate is used exclusively as a high energy plasticizer for propellants. Current U. S. production capacity is 25,000 lb/year. The only Army use of this chemical in the past several years has been three 55 gallon drums. This material was produced and used at RAAP for formulation of M-37 propellant.

Due to the limited use of diethyleneglycol dinitrate by the Army, this compound should be a low priority for further evaluation by the Army. However, if future plans call for large production of M-37, then a detailed evaluation of the toxicological and environmental hazards of this compound would be warranted.

#### 2-Nitrodiphenylamine

2-nitrodiphenylamine is widely used as a stabilizer in double-base solid propellant formulations. It is found in the formulations in concentrations of 0.9 to 3.0%. Radford is the only operational Army Ammunition Plant which is using 2-nitrodiphenylamine. Badger and Sunflower also use this compound when they are operational.

Current use rate of 2-nitrodiphenylamine at Radford AAP is ~6000 lb/month. At full mobilization the Radford AAP use rate for this compound is 6000 - 7000 lb/month. It is expected that at full mobilization the usage of 2-nitrodiphenylamine at the Badger and Sunflower AAPs would be approximately the same as at Radford AAP. Thus a total of 252,000 lb/year of 2-nitrodiphenylamine could be used by the Army.

There is only one civilian producer of 2-nitrodiphenylamine. The civilian capacity is estimated at ~250,000 lb/year. The only civilian use of 2-nitrodiphenylamine is as a chemical intermediate in the dye industry. However, civilian companies that make solid rockets could purchase some of this compound. The extent of these purchases is unknown.

At current production levels, Radford utilizes ~40% of the estimated civilian production capacity of 2-nitrodiphenylamine. With three plants

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at full mobilization, the Army would purchase ~100% of the estimated civilian production capacity of this chemical. Under current operational conditions, the Army may be one of the main polluters of 2-nitrodiphenylamine. The percentage of the total 2-nitrodiphenylamine pollution emanating from Army propellant manufacturing is impossible to determine, due to the unavailability of civilian production statistics.

Limited mammalian toxicology studies indicate 2-nitrodiphenylamine is not very toxic in acute doses (LD50 for rats = 6.15 g/kg). Limited studies concerning the toxicity of 2-nitrodiphenylamine to fish and invertebrates show that this compound is highly toxic to aquatic organisms with LC50's ranging from 1.8 to 5.6 ppm. Reaction of 2-nitrodiphenylamine in the environment could lead to more toxic compounds.

Although 2-nitrodiphenylamine is not a military unique compound, the military is one of the major users and polluters of this chemical. Preliminary evidence indicates a high potential environmental danger from 2-nitrodiphenylamine. It is, therefore, recommended that 2-nitrodiphenylamine be included in the Phase II detailed toxicological and environmental studies.

#### N-Nitrosodiphenylamine

N-nitrosodiphenylamine is not used by the Army in its munitions production. This compound is formed in solid propellants as a result of the reaction of diphenylamine with NO. The NO is produced from the degradation of nitrate ester explosives in the propellant. N-nitrosodiphenylamine is present in the effluents from propellant manufacture. Maximum discharges of this compound at full mobilization are estimated to be 360-600 lb/year. However, it could be formed in the environment by the action of microorganisms. Studies have indicated that N-nitrosamine can be formed microbially from diphenylamine and nitrate.

N-nitrosodiphenylamine is produced commercially by four companies. Its only use is as a vulcanization retarder for rubber. However, N-nitrosodiphenylamine is being replaced by steroid-type retarders by the rubber industry.

The toxicity of N-nitrosodiphenylamine in acute doses is low (LD50 for rats is 5360 mg/kg). This compound has been tested for carcinogenic potency. It has been found to be non-carcinogenic. The aquatic toxicity of this compound is unknown.

From the information evaluated in this study it is concluded that N-nitrosodiphenylamine is not a military unique chemical. Any potential effects of this compound on the aquatic ecosystem would be overshadowed by those of diphenylamine. Therefore, N-nitrosodiphenylamine should be a low priority for further study by the Army.

## The Phthalate Esters

Diethyl-, dibutyl- and diethylhexyl phthalate are used as plasticizers in the manufacture of solid propellants at Radford, Badger, Sunflower and Indiana Army Ammunition Plants (AAP). Currently only Radford and Indiana are operational. Of the phthalate esters, dibutyl phthalate is the largest volume propellant additive.

At current production rates, Radford uses 344,000 lb/year of this compound, primarily for the M-1 formulation. At full mobilization, 2.5 million lb/year of dibutyl phthalate would be needed by Radford AAP alone. Estimated discharges of dibutyl phthalate to the New River at full mobilization are 700 to 2150 lb/month.

Diethyl phthalate is used exclusively in the N-5 and M-8 propellant formulations. Current use rate of diethyl phthalate is 228,000 lb/year. Radford is currently operating at full production capacity of these propellants. Discharge of diethyl phthalate to the New River are estimated at 63 to 380 lb/month.

Diethylhexyl phthalate is seldom used by Radford. Only 22,000 lb of this chemical has been formulated into propellants over the last 10 years.

The phthalate esters are widely used throughout the civilian community. Over 1,043 million lb of phthalate esters were produced in the United States in 1976. The 1976 production of the individual esters was

- diethylhexyl phthalate	296.7 million lb
- dibutyl phthalate	13.7 million lb
- diethyl phthalate	16.1 million lb

Each of these esters is used as a plasticizer for different materials. Diethylhexyl phthalate is used in PVC plastics, dibutyl phthalate in nitrocellulose and polyvinyl acetate emulsions and diethyl phthalate in cellulose acetate plastics.

The acute toxicity of the phthalate esters to mammals is low with LD50's ranging from 1 to 8 g/kg. Some subtle biochemical changes are observed in mammals exposed to phthalate esters over long periods of time. The esters have been shown to be noncarcinogenic. However, they have mutagenic and teratogenic potential at high doses.

The phthalate esters are wide spread throughout the environment. They are found in river and ocean water, sediment and biota. Diethylhexyl phthalate is the most abundant of the phthalate esters in the environment. The phthalate esters are fairly toxic to aquatic organisms with a 96-hour LC50's in the low ppm. Some bioaccumulation of these compounds occurs, however, they are actively metabolized by most organisms.

From the information evaluated during this study, it is concluded that the phthalate esters are not military unique chemicals. Dibutyl phthalate appears to be the most widely used phthalate ester by the military. At current propellant production rate, the military use of this chemical is only a small percentage of the civilian production. However, if all four propellant plants were operating at full mobilization levels, military use of dibutyl phthalate could be as high as 73% of the 1976 civilian production of this chemical. Dibutyl phthalate discharges would be as high as 4160 lb/month from Radford AAP at full mobilization. At this discharge level, this chemical would be toxic to aquatic life. Further evaluation of the environmental fate of dibutyl phthalate by the Army may be warranted. However, the proposed biotreatment facility should adequately remove this compound from Radford's effluents. Thus, this chemical should be a low priority for further study.

Diethyl phthalate is not used or discharged in amounts harmful to the environment. It is also a relatively low use chemical in propellant manufacture. Based on these facts and the ease with which diethyl phthalate is biodegraded, this chemical should be a low priority for further study.

The Army's utilization of diethylhexyl phthalate is insignificant when compared to that of the civilian community. Therefore, diethylhexyl phthalate should be a low priority for further study.

#### Triacetin

Triacetin is used as a plasticizer in solid propellant formulations. These formulations contain 3.25 to 11.0% triacetin. At the present time only Radford AAP uses triacetin. Current use rate is ~43,000 lb/year. At full mobilization 150,000 lb/year would be used by Radford. Sunflower and Badger would use similar amounts at full mobilization.

Estimated losses of triacetin from current propellant manufacture are between 180 and 540 lb/month. At full mobilization, up to 2000 lb/month could be lost at each plant using triacetin. Since this compound is readily soluble in water, virtually all the triacetin lost will be in the waste streams.

Triacetin is produced in the United States by three manufacturers. Current production capacities are estimated at 1 million lb/year. Triacetin has a wide variety of uses in the civilian community including a plasticizer in cigarette filters, a solvent and carrier in pharmaceutical preparations, a solvent and fixative in perfumes and flavors, etc. Because of the widespread use of triacetin in disposable items, the civilian pollution of triacetin is also expected to be widespread.

Mammals exhibit a low toxic response to triacetin. However, aquatic organisms and invertebrates are fairly sensitive to this chemical. At full mobilization, significant effects on the local aquatic population near Radford, Sunflower and Badger could occur. Microorganisms should readily degrade this compound, precluding any widespread damage to the ecosystem.

At current production levels, the Army uses only 4% of the triacetin civilian production capacity. At full mobilization, the Army usage of this chemical could be as high as 45% of the civilian capacity. Although the Army use rate of triacetin could be high under emergency conditions, this chemical is not a military unique compound.

The only Army problem with triacetin appears to be potential local aquatic effects. The planned biotreatment facility at Radford should adequately remove this compound from Radford's waste streams. From these findings it appears that triacetin has a low priority for inclusion in the Phase II work. If it were to be included, the study should be limited to environmental toxicology and fate.

#### Lead Salicylate

Lead salicylate is used as a burning rate modifier in solvent and solventless double base propellants. This compound is currently only used at Radford Army Ammunition Plant. At current production rates, 3000 lb of lead salicylate are used at Radford AAP each month. This usage represents full production capacity of the propellants employing lead salicylate in their formulations. Losses of lead salicylate to the environment from Radford AAP operations are estimated at 45-150 lb/month.

Lead salicylate is manufactured by one civilian firm. Potential production capacities for this chemical are estimated at ~1 million lb/year. In the civilian market, lead salicylate is used as a stabilizer in flooring and other vinyl compounds requiring good light stability.

Lead salicylate is toxic to mammals. It is readily absorbed through the skin. The aquatic toxicity of this compound is unknown. However, due to the limited solubility of lead salicylate, the aquatic toxicity is probably low.

The absence of production statistics makes an evaluation of the military versus civilian usage difficult. However, it is estimated that the Army used ~1/3 - 1/2 of the lead salicylate produced by the civilian community. The Army propellant manufacture is probably the main source of environmental pollution of this compound. Therefore, it is recommended that lead salicylate be included in the detailed Phase II toxicological and environmental evaluations.

### Lead Stearate

Lead stearate is used in the berrite grains and the ROLAND propellant as a burning rate modifier. The propellants are not currently being produced by the Army. If these propellants were produced at full capacity, 500 lb/month of lead stearate would be used at RAAP.

The civilian production of lead stearate was 1,254,000 lb/year in 1976. This compound is used as a general purpose and high pressure lubricant and heat stabilizer for PVC compounds. Due to its many civilian uses, pollution from civilian uses of lead stearate is expected to be widespread.

Lead stearate is moderately toxic to mammals. The toxicity of this compound to aquatic organisms is unknown. However, due to its limited solubility, the aquatic toxicity should be low unless it is hydrolyzed to free lead.

Lead stearate is not a military unique chemical. Because of the limited use of this compound in propellant production, further studies by the Army should be of low priority.

### Lead Resorcyate

Lead resorcyate was developed in 1965 by NL Industries. Information on this compound is non-existent in the literature. There are no reported civilian uses of lead resorcyate. Thus it appears that the Army's propellant manufacture accounts for all civilian production of this compound.

Lead resorcyate is a military unique chemical. Further studies on this compound by the Army are recommended. These studies should include

- A Phase II detailed toxicological and environmental evaluation
- Determination of some of the physical and chemical properties of this compound if they can not be obtained from the manufacturer
- Sampling and analysis of sediment and biota at Radford AAP to determine the amount of accumulation
- Aquatic toxicity and bioaccumulation studies if the Phase II study indicates the need for this research
- Mammalian skin toxicity studies.



## FOREWORD

This report details the results of a preliminary problem definition study on propellant related chemicals. The purpose of this study was to determine the Army's responsibility for conducting further research on these chemicals in order to determine their toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on these propellant related chemicals, the military and civilian usage and pollution of these substances were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

The propellant related chemicals represent 10 of the 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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## I. GENERAL OVERVIEW OF PROPELLANT MANUFACTURE, LOADING AND DISPOSAL

Chemical additives are used in conjunction with primary explosives in the manufacture of propellants. These additives are predominantly used as stabilizers, modifiers or plasticizers. Some function as flash suppressants or barrel coolants. Specific compounds of this type which are of concern in this study include:

- Ethyl centralite
- Diphenylamine
- Diethyleneglycol dinitrate
- 2-nitrodiphenylamine
- N-nitrosodiphenylamine
- Phthalate esters
- Triacetin
- Lead salicylate
- Lead stearate
- Lead resorcyate
- Barium nitrate

N-nitrosodiphenylamine is not added to the propellant formulations, but appears as a degradation product of diphenylamine.

### A. Propellant Manufacture

Propellants are produced by mixing primary explosives such as nitrocellulose, nitroglycerin or nitroguanidine with additives such as those listed above. Propellants are characterized as single base, double base or composite (triple base or multibase). Single base propellants contain only one primary explosive, nitrocellulose. Double base propellants contain nitroglycerin as well as nitrocellulose. Composite propellants contain these two primary explosives and at least one additional explosive such as nitroguanidine or HMX. Propellants are manufactured by either a solvent process or a solventless process.

#### 1. Manufacturing Facilities

Propellants are currently produced in only two facilities, Radford Army Ammunition Plant (RAAP) and Indiana Army Ammunition Plant (InAAP). Two other facilities, Badger AAP (BAAP) and Sunflower AAP (SAAP), are capable of producing propellants; but the plants are inactive. Table I-1 lists the propellant-related functions of these plants.



Table I-1. Propellant Manufacturing Facilities.

<u>Facility</u>	<u>Function</u>
Badger AAP Baraboo, Wisconsin	single base propellants ball powder solventless rocket grains
Radford AAP Radford, Virginia	single base propellants double base propellants composite propellants LAP* missile propellants LAP* large rocket propellants LAP* cannon propellants
Sunflower AAP Lawrence, Kansas	single base propellants double base propellants composite propellants solventless rocket grains
Indiana AAP Charlestown, Indiana	propellant charges LAP* propellant charges

\*LAP = Load, Assembly and Pack

The Radford AAP has capacity for production of about 12 million lb/month of propellants. This plant is currently operating at about 20% of capacity. During December 1977, the total production of propellants was about 2.6 million lb. This figure includes about 870,000 lb of single base propellants (solvent process), predominantly the M-1 formulation. Also produced were 350,000 lb of double base propellants by the solvent process and 240,000 lb by the solventless process. The production of multibase propellants was approximately 1,140,000 lb, all by the solvent process.

These propellants were produced in the "C" propellant line and the No. 4 Roll Powder Area. The location of these areas is shown on the map (Figure I-1). The Roll Powder plant was used to produce double base propellants by the solventless process. All other propellants were produced in the "C" line facilities. As may be seen in Figure I-1, the "C" line consists of a nitrating area, cotton area, green powder plant, solvent recovery area and the air and water drying area.

## 2. Compounds and Formulations Used

The additive compounds listed earlier, as well as others not considered in this study, are used in various propellant formulations. Table I-2 lists the facilities which use these various modifiers, stabilizers and plasticizers.

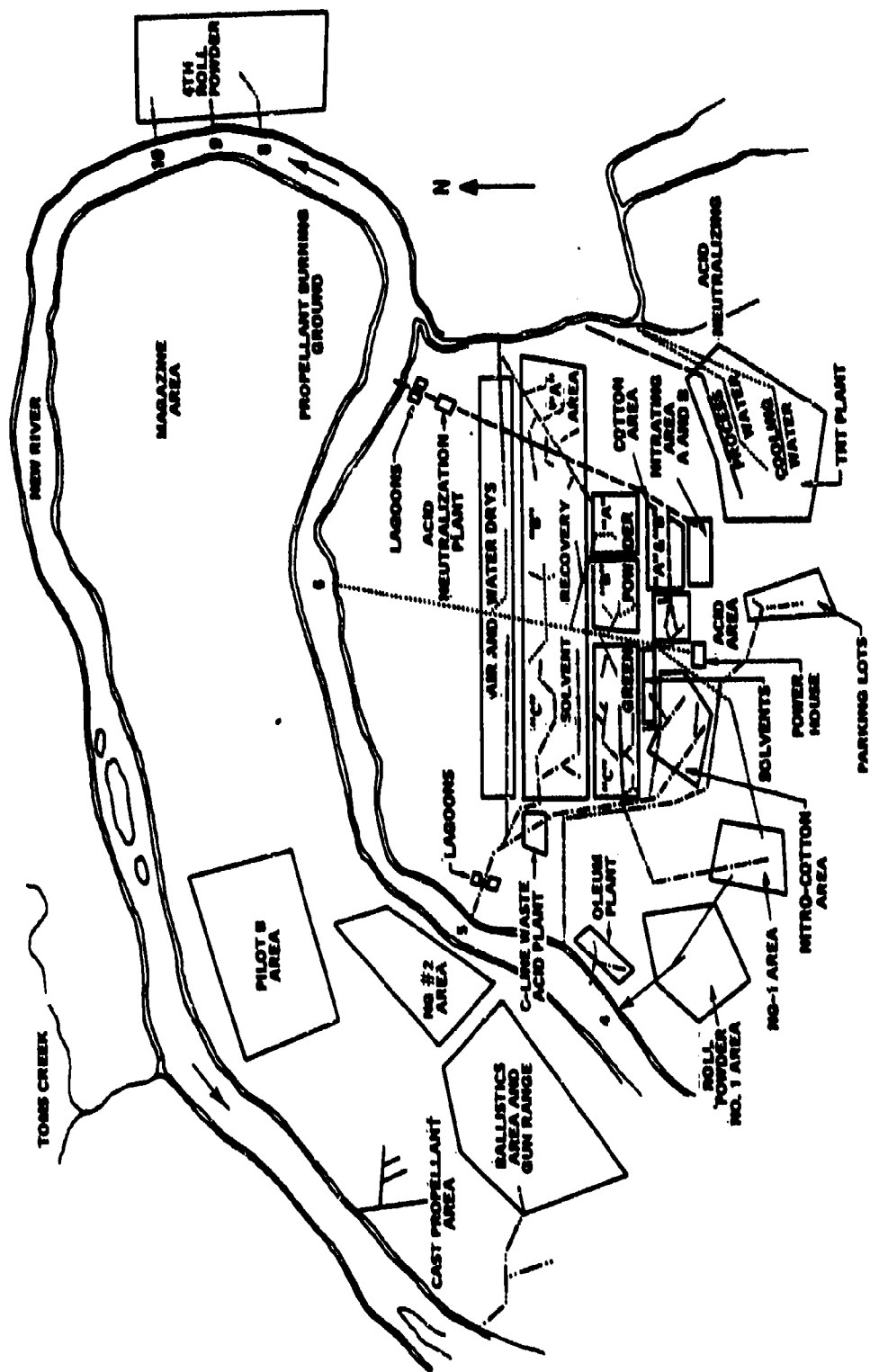


Figure f-1. Map of Radford Army Ammunition Plant.

Table I-2. Army Ammunition Plants Which Use the Various Propellant Additives.

<u>Additive</u>	<u>Facility</u>			
	BAAP	RAAP	SAAP	InAAP
Ethyl centralite	x	x	x	x
Diphenylamine	x	x	x	x
Diethyleneglycol dinitrate		x		
2-nitrodiphenylamine	x	x	x	
N-nitrosodiphenylamine	x	x	x	x
Diethyl phthalate	x	x	x	x
Dibutyl phthalate	x	x	x	x
2-ethylhexyl phthalate		x		
Triacetin	x	x	x	
Lead salicylate	x	x	x	
Lead stearate	x	x	x	
Lead resorcyate	x	x	x	
Barium nitrate		x		

Over 40 different propellant formulations are produced. Their constituents and compositions are given in Table I-3. Almost all of these propellants include at least one of the additives of concern to this study in their formulations. The ranges of percentages used in the various propellants are listed in Table IV-4.

Table I-4. Percentage of Additives in Propellant Formulations.

<u>Additive</u>	<u>Percentage</u>
Ethyl centralite	0.02-6.5
Diphenylamine	0.5-1.7
Diethyleneglycol dinitrate	*
2-nitrodiphenylamine	0.9-2.5
Diethyl phthalate	2.5-10.5
Dibutyl phthalate	2.0-6.0
Triacetin	3.3-11.0
Lead salicylate	2.8-3.3
Lead stearate	0.1
Lead resorcyate	2.8-3.3
Barium nitrate	0.6-1.0

\*Total of 3-55 gallon drums used one time only at RAAP to produce M-37 propellant

### 3. Propellant Manufacturing Processes

#### a. Solvent Process

The majority of single base, double base and composite propellants are manufactured by the solvent process. This process involves numerous operations as shown in Figure I-2. The figure describes the manufacture of a single base propellant. However, the solvent process for producing double base or composite propellants is similar.

In the first step, nitrocellulose, produced from nitration of cotton linters or wood pulp, is dried by wringing (Military Explosives, 1967). The nitrocellulose, containing ~28% moisture, is then dehydrated by the addition of 95% ethanol. After dehydration, pressure is applied to the material to yield a block containing ~75% nitrocellulose and ~25% of 90% ethanol.

The wet block is broken up and transferred to a mixer. Ether is added to the extent of about 2/3 of the weight of dry nitrocellulose. Additives such as diphenylamine and dibutyl phthalate are generally mixed with the ether before it is added. After the ether is added, any other propellant modifiers are added. The ingredients are mixed for about one hour.

The propellant mixture is pressed at about 3000 psi to form a block. The propellant is then squeezed through a series of screens and perforated plates. It emerges from this step in a form resembling macaroni. The material is again pressed into block form, then extruded through dies form cords of the desired final diameter. The cords are cut into pieces of predetermined length. This process is called graining.

The remaining solvents are then recovered. The grains are water dried by placing them in warm water. This reduces the solvent content to 1 to 5%. Air drying then removes the surface moisture.

Finally, the propellant is screened to remove dust and grain clusters. It is sometimes glazed or coated with graphite. The batches of propellants are blended to insure uniformity of the lot, then packed for shipping to the loading operations.

#### b. Solventless Process

In the solventless process (Patterson *et al.*, 1976), a premix is made from nitrocellulose and nitroglycerin plus the desired additives. The premix is dispersed in water as a carrier. Most of the water is removed by centrifuging. The paste thus formed is air dried, then mixed with any other ingredients in a tumble blender.

The final mix is passed through roll calenders to form a homogeneous sheet. Several sheets are combined and rerolled to yield a single sheet of the desired thickness. The sheets are cut into strips. The strips are rolled up and fed into a finishing press. There is minimal shrinkage of

Table I-3. Propellant Formulations Produced at Radford Army

Formulation	Nitrocellulose	Nitroguan	Nitroglycerin	Nitrosamidine	Isobutyl Cellulose	Bisphenolamine	Isobutyl- diphenylamine	Bisethyl Phthalate	Bisethyl Phthalate	Triethyl amine
W-10	50.0				0.550.7					
W-10-1		0.55			1.050.7					
W-10-2	50.0				1.050.7					
W-10-3	50.0				0.5	0.5 to 1.5				
W-10-4	50.0				1.050.7	0.1			1.050.7	
W-10-5	50.0				1.050.7	0.1			1.050.7	
W-10-6	50.0				1.050.7	0.1			1.050.7	
W-10-7	50.0				1.050.7	0.1			1.050.7	
W-10-8	50.0				1.050.7	0.1			1.050.7	
W-10-9	50.0				1.050.7	0.1			1.050.7	
W-10-10	50.0				1.050.7	0.1			1.050.7	
W-10-11	50.0				1.050.7	0.1			1.050.7	
W-10-12	50.0				1.050.7	0.1			1.050.7	
W-10-13	50.0				1.050.7	0.1			1.050.7	
W-10-14	50.0				1.050.7	0.1			1.050.7	
W-10-15	50.0				1.050.7	0.1			1.050.7	
W-10-16	50.0				1.050.7	0.1			1.050.7	
W-10-17	50.0				1.050.7	0.1			1.050.7	
W-10-18	50.0				1.050.7	0.1			1.050.7	
W-10-19	50.0				1.050.7	0.1			1.050.7	
W-10-20	50.0				1.050.7	0.1			1.050.7	
W-10-21	50.0				1.050.7	0.1			1.050.7	
W-10-22	50.0				1.050.7	0.1			1.050.7	
W-10-23	50.0				1.050.7	0.1			1.050.7	
W-10-24	50.0				1.050.7	0.1			1.050.7	
W-10-25	50.0				1.050.7	0.1			1.050.7	
W-10-26	50.0				1.050.7	0.1			1.050.7	
W-10-27	50.0				1.050.7	0.1			1.050.7	
W-10-28	50.0				1.050.7	0.1			1.050.7	
W-10-29	50.0				1.050.7	0.1			1.050.7	
W-10-30	50.0				1.050.7	0.1			1.050.7	
W-10-31	50.0				1.050.7	0.1			1.050.7	
W-10-32	50.0				1.050.7	0.1			1.050.7	
W-10-33	50.0				1.050.7	0.1			1.050.7	
W-10-34	50.0				1.050.7	0.1			1.050.7	
W-10-35	50.0				1.050.7	0.1			1.050.7	
W-10-36	50.0				1.050.7	0.1			1.050.7	
W-10-37	50.0				1.050.7	0.1			1.050.7	
W-10-38	50.0				1.050.7	0.1			1.050.7	
W-10-39	50.0				1.050.7	0.1			1.050.7	
W-10-40	50.0				1.050.7	0.1			1.050.7	
W-10-41	50.0				1.050.7	0.1			1.050.7	
W-10-42	50.0				1.050.7	0.1			1.050.7	
W-10-43	50.0				1.050.7	0.1			1.050.7	
W-10-44	50.0				1.050.7	0.1			1.050.7	
W-10-45	50.0				1.050.7	0.1			1.050.7	
W-10-46	50.0				1.050.7	0.1			1.050.7	
W-10-47	50.0				1.050.7	0.1			1.050.7	
W-10-48	50.0				1.050.7	0.1			1.050.7	
W-10-49	50.0				1.050.7	0.1			1.050.7	
W-10-50	50.0				1.050.7	0.1			1.050.7	
W-10-51	50.0				1.050.7	0.1			1.050.7	
W-10-52	50.0				1.050.7	0.1			1.050.7	
W-10-53	50.0				1.050.7	0.1			1.050.7	
W-10-54	50.0				1.050.7	0.1			1.050.7	
W-10-55	50.0				1.050.7	0.1			1.050.7	
W-10-56	50.0				1.050.7	0.1			1.050.7	
W-10-57	50.0				1.050.7	0.1			1.050.7	
W-10-58	50.0				1.050.7	0.1			1.050.7	
W-10-59	50.0				1.050.7	0.1			1.050.7	
W-10-60	50.0				1.050.7	0.1			1.050.7	
W-10-61	50.0				1.050.7	0.1			1.050.7	
W-10-62	50.0				1.050.7	0.1			1.050.7	
W-10-63	50.0				1.050.7	0.1			1.050.7	
W-10-64	50.0				1.050.7	0.1			1.050.7	
W-10-65	50.0				1.050.7	0.1			1.050.7	
W-10-66	50.0				1.050.7	0.1			1.050.7	
W-10-67	50.0				1.050.7	0.1			1.050.7	
W-10-68	50.0				1.050.7	0.1			1.050.7	
W-10-69	50.0				1.050.7	0.1			1.050.7	
W-10-70	50.0				1.050.7	0.1			1.050.7	
W-10-71	50.0				1.050.7	0.1			1.050.7	
W-10-72	50.0				1.050.7	0.1			1.050.7	
W-10-73	50.0				1.050.7	0.1			1.050.7	
W-10-74	50.0				1.050.7	0.1			1.050.7	
W-10-75	50.0				1.050.7	0.1			1.050.7	
W-10-76	50.0				1.050.7	0.1			1.050.7	
W-10-77	50.0				1.050.7	0.1			1.050.7	
W-10-78	50.0				1.050.7	0.1			1.050.7	
W-10-79	50.0				1.050.7	0.1			1.050.7	
W-10-80	50.0				1.050.7	0.1			1.050.7	
W-10-81	50.0				1.050.7	0.1			1.050.7	
W-10-82	50.0				1.050.7	0.1			1.050.7	
W-10-83	50.0				1.050.7	0.1			1.050.7	
W-10-84	50.0				1.050.7	0.1			1.050.7	
W-10-85	50.0				1.050.7	0.1			1.050.7	
W-10-86	50.0				1.050.7	0.1			1.050.7	
W-10-87	50.0				1.050.7	0.1			1.050.7	
W-10-88	50.0				1.050.7	0.1			1.050.7	
W-10-89	50.0				1.050.7	0.1			1.050.7	
W-10-90	50.0				1.050.7	0.1			1.050.7	
W-10-91	50.0				1.050.7	0.1			1.050.7	
W-10-92	50.0				1.050.7	0.1			1.050.7	
W-10-93	50.0				1.050.7	0.1			1.050.7	
W-10-94	50.0				1.050.7	0.1			1.050.7	
W-10-95	50.0				1.050.7	0.1			1.050.7	
W-10-96	50.0				1.050.7	0.1			1.050.7	
W-10-97	50.0				1.050.7	0.1			1.050.7	
W-10-98	50.0				1.050.7	0.1			1.050.7	
W-10-99	50.0				1.050.7	0.1			1.050.7	
W-10-100	50.0				1.050.7	0.1			1.050.7	

Ammunition Plant (Hercules, Inc., 1977).

D-203 or Lead Salicylate	Lead Stearate	D-203 or Lead Benzenesulfate	Barium Nitrate	Charcoal	Graphite	Carbon Black	Other
				0.450.3			Potassium Nitrate 44.11 Sulfur 0.100.3 Di-n-Propyl Sulfate 1.000.3 Lead Carbonate 1.000.3 Potassium Sulfate 1.250.3 Potassium Nitrate 0.1
				0.1 Type 1 0.1 Type 2 0.01			Potassium Sulfate 30.0
				0.4			Dimethylsiloxane 0.5 to 10.0 Potassium Sulfate 0.10 to 1.0 Dimethylsiloxane 10.002.0 Potassium Sulfate 1.000.3 Dimethylsiloxane 10.002.0 Potassium Sulfate 1.000.3 Dimethylsiloxane 10.002.0 Potassium Sulfate 1.000.3
				0.21			Dimethylsiloxane 10.002.0 Potassium Sulfate 1.000.3
2.5				0.0310.00			Potassium Sulfate 1.000.3 N-101 1.5
2.01.25		2.01.25		0.0410.01			Carbon 1 0.0410.01
						0.1 1.7	Potassium Perchlorate 7.0 Potassium Perchlorate 0.05
				0.7510.7	0.110.1 0.110.1		Potassium Nitrate 0.710.33
		2.33		0.34 (w/Carbon)			Potassium Sulfate 0.7500.1 Carbon 1 0.34 (w/graphite) Potassium Nitrate 1.2510.33 Potassium Nitrate 1.2500.33
2.5							N-101 1.2 Sundellite Wax 0.2 Sundellite Wax 0.1 Di-n-Propyl Adipate 0.4 C-201 2.4 Di-n-Propyl Adipate 1.0 C-201 2.0
2.5		0.3					Sundellite Wax 0.1 Di-n-Propyl Adipate 2.0 C-201 1.5 N-101 (as Salicylate) 1.0 Al 1.5
2.5		Type II 0.3				0.03	Sundellite Wax 0.03 Di-n-Propyl Adipate 2.0 C-201 1.5 N-101 (as Salicylate) 1.0 Al 1.5
							Sundellite Wax 0.1 Di-n-Propyl Adipate 1.2 C-201 2.5 Al 2.5
							Sundellite Wax 0.15 Di-n-Propyl Adipate 3.03 C-201 2.0
					0.7		Crystalline 0.10.1 Potassium Sulfate 1.000.3 Potassium Nitrate 0.710.33 N-101 1.0
1.2					0.15		
1.2							N-101 2.0 Carbon 1 0.15
1.2		2.33			0.33	0.03	Acetone 10.001.3 Dimethylsiloxane 17.001.0 N-101 75.0 to 75.7 Di-n-Propyl Sebacate 21.3 Sulfur 0 to 2.000

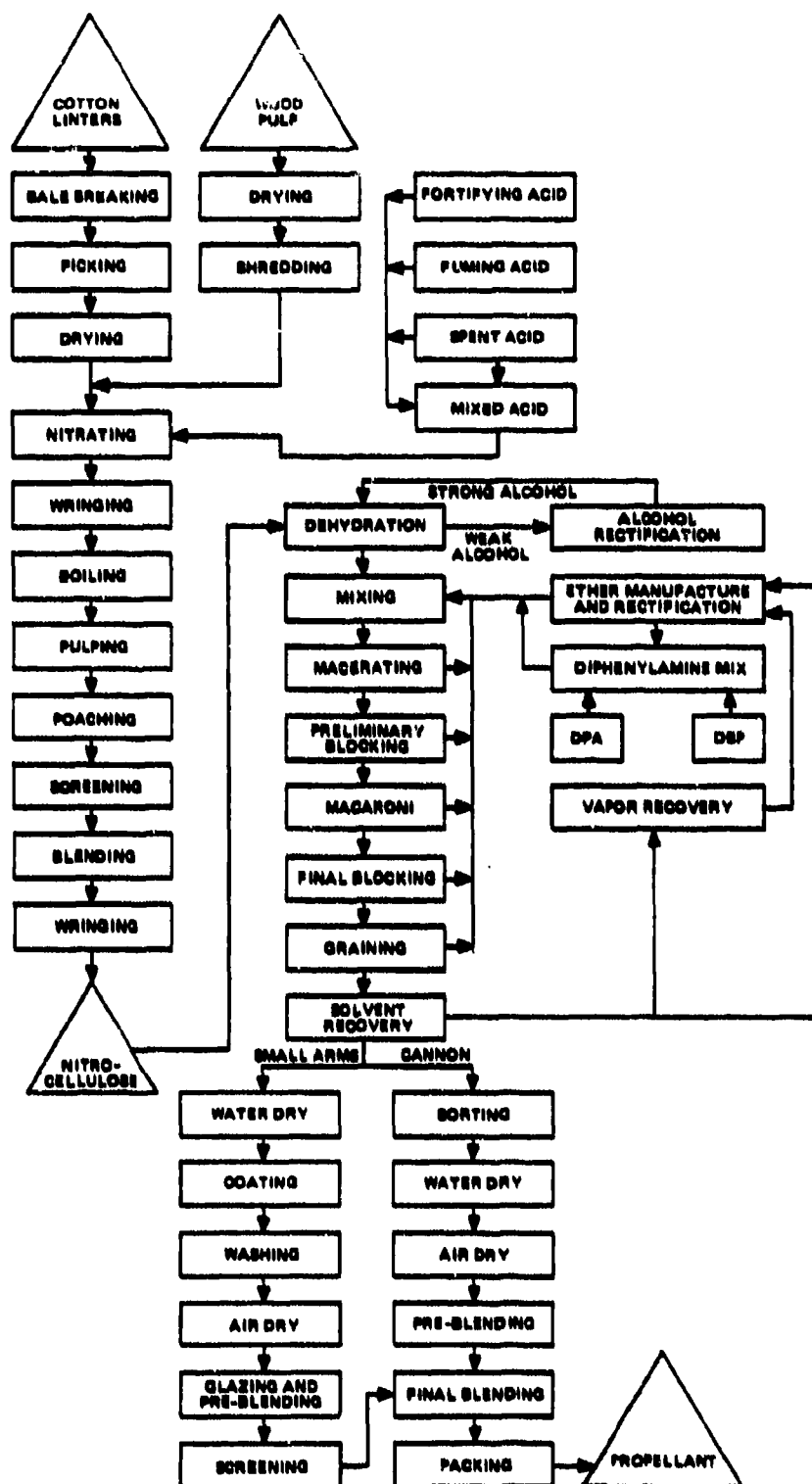


Figure I-2. Schematic of Propellant Manufacture by the Solvent Process.

the propellant strands during final processing as it contains no volatile material.

c. Ball Powder

Ball powder is a single base propellant produced by the solvent process. However, the propellant is formed into spheres of 0.030 inches diameter or less. The processing steps are significantly different from conventional propellant manufacturing as described above.

Figure I-3 is a schematic diagram of the ball powder process (Patterson *et al.*, 1976). Single base propellant is ground in a water slurry. It is extracted with benzene, then dissolved in ethyl acetate. The ethyl acetate forms a separate phase on top of the slurry water. The two phases are emulsified by agitation. Collagen is added to prevent coalescence of the globules. Sodium sulfate is added to draw water out of the globules. The temperature is raised to 69°C causing the ethyl acetate solvent to boil off. The globules slowly harden into firm spheres suspended in the water phase.

The spheres are coated with DNT to retard their initial burning rate. The spheres, still in water slurry, are passed through rollers to make them slightly elliptical. They are then filtered and dried. The final processing steps are to glaze the spheres with a thin coating of graphite, screen them and package them for shipment.

d. Current Propellant Production at Radford AAP

During December 1977, the following propellants were produced at RAAP:

<u>Propellant</u>	<u>Type</u>	<u>Quantity, thousand lb</u>
Benite	Single-solvent	25
M-1	Single-solvent	817
M-10	Single-solvent	29
ARP	Double-solvent	100
M-7	Double-solvent	6
M-26	Double-solvent	242
M-8	Double-solventless	32
NOSIH-AM-2	Double-solventless	44
M-36	Double-solventless	27
N-5	Double-solventless	134
M-30	Multibase-solvent	683
M-30A2	Multibase-solvent	453

Of these propellants, the M-8, M-36, N-5, ARP and NOSIH-AM-2 were produced at essentially full mobilization rates. The others ranged from 10 to 20 percent of full mobilization capacity.





a. Current Use Rates of Chemical Additives

At current (December 1977) production rates, RAAP consumes the following amounts of the listed additives:

<u>Additive</u>	<u>Current use rate, lb/mo.</u>
Barium nitrate	5,200
Ethyl centralite	31,226
Diphenylamine	10,000
2-nitrodiphenylamine	4,600
Diethyl phthalate	19,000
Dibutyl phthalate	28,000
Triacetin	5,900
Lead salicylate	3,000
Lead resorcyate	670
Lead stearate	0

f. Historic Production and Chemical Usage at Radford AAP

Table I-5 lists the production rates for each propellant manufactured at Radford AAP during the years 1968-1977. The annual purchases of additive chemicals during this period are shown in Table I-6.

4. Effluent Streams

Process water is used for all propellant production processes at RAAP. Much of this water is recycled, but some leaves the process and ultimately enters the New River. Current (December 1977) propellant operations produce effluents which enter the river at points 4, 5, 6, 8, 9 and 10 on Figure I-1. Waste streams associated with propellant production are described below: (Cairns and Dickson, 1971); Smith and Dickensen, 1972)

1. C-line waste water (Figure I-1, point 4)

This stream contains wastes from the nitroglycerin and nitrocotton production areas, solvent recovery areas, water dry buildings and solvents area.

2. General purpose sewer, 48 in. (Figure I-1, point 6)

This source collects effluents from the green powder production areas, solvent recovery areas and the water dry buildings.

3. Solvent recovery (Figure I-1, point 5)

Discharges from the green powder production areas, solvent recovery areas and water dry areas are contained in this waste stream.

Table I-5. Production History at Radford AAP\*  
(Watts, 1978).

Propellant	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977
M-1	86,898.0	71,595.9	53,383.0	48,881.2	51,132.3	56,638.3	72,421.2	34,622.7	9,344.9	8,571.2
M-6	30,173.4	12,971.1	4,125.4	119.9	80.1	81.4	203.3	132.4	606.4	817.9
M-10	0.2	-	-	0.6	242.4	281.3	236.2	170.6	-	22.4
M-6+2	-	-	-	-	-	33.4	16.1	3.0	85.1	-
Bealite	49.4	89.2	168.2	54.0	97.7	57.1	39.7	81.5	97.5	99.4
CBI	1,532.6	1,671.1	630.6	478.4	741.5	739.1	782.6	-	-	-
BS-MACO	1,851.5	22,261.2	3,772.9	-	204.4	1,908.4	84.2	48.7	1,480.1	1,793.1
THR 5010	-	-	538.6	285.4	119.4	-	-	-	336.0	89.4
AMM	30.0	-	-	-	118.5	193.9	291.9	-	-	337.8
AMP	-	-	-	-	-	-	-	-	-	-
M-7	301.6	440.0	124.7	45.5	60.6	136.3	87.4	30.5	-	-
M-26	1,167.3	818.6	99.2	1,487.4	857.7	50.3	1,664.5	2,978.3	194.2	2,370.8
M26Z1	2,358.8	4,424.4	8.9	26.2	11396.2	384.5	1,038.0	481.1	392.7	888.1
PLJ	-	-	-	41.8	111.4	-	200.5	387.6	194.3	187.3
M-8	3,920.4	1,994.9	111.1	174.0	354.6	291.1	111.4	109.2	-	52.7
M-5	2,898.2	137.3	39.0	-	-	-	59.8	382.3	1,044.4	2,281.6
J-14	-	0.6	-	1.1	1.6	1.7	9.6	-	-	11.4
ROSIN-AA-2	-	-	12.2	-	25.6	-	-	-	-	4.7
ROSIN-AA-6	-	-	11.7	78.2	1,192.7	2,011.9	2,011.9	1,228.9	50.6	-
ROSIN-AH-2	-	-	-	-	-	-	4.3	16.4	91.9	71.2
M-36	-	-	-	-	-	-	-	-	125.9	504.9
M-12	69.2	7.5	35.4	-	33.6	57.9	96.9	80.1	25.9	37.8
H30	14,622.8	8,278.7	6,135.6	19,161.4	11,772.5	3,669.7	6,448.6	11,403.2	7,902.0	8,803.4
H30A1	-	446.8	-	156.2	2,378.8	1,301.2	183.0	21.4	105.3	1,081.6
H30A2	-	-	-	-	-	-	-	-	2,671.7	2,865.2

\*All numbers in thousand lb

Table I-6. Propellant Additives - Annual Purchases, 1968-1977\*  
(Watts, 1978).

Material	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977
Barium nitrate	14,400	3,900	0	13,500	750	1,200	22,850	15,800	5,400	14,700
Acetylene black	0	0	0	0	0	0	0	172	150	150
Ethyl centralite	511,175	695,950	140,350	233,450	444,325	60,725	399,469	356,650	285,268	304,649
Diphenylamine	1,229,250	950,100	772,600	548,800	546,350	767,600	839,990	337,550	94,000	133,200
2-nitrodiphenylamine	262,800	40,000	0	8,900	79,800	57,250	101,400	12,500	32,200	97,100
Diethyl phthalate	987,100	282,500	6,000	0	0	0	6,000	63,880	133,360	236,580
Dibutyl phthalate	5,376,890	3,854,218	2,570,860	2,377,790	2,538,160	2,700,910	3,727,418	1,425,700	434,000	349,800
Dioctyl phthalate	6,300	0	0	0	6,300	9,450	0	0	0	0
Triacetin	80,000	80,000	0	0	39,830	198,560	160,690	41,980	43,280	43,040
Lead salicylate	206,800	85,600	0	0	0	28,000	66,000	10,200	24,200	39,600
Lead stearate	1,500	5,100	2,250	0	6,450	10,000	0	844	733	250
Lead beta resorcyate	189,300	149,521	398	692	14,355	30,934	24,034	12,620	23,537	5,266

\*All numbers in lb

4. Rolled powder area wastes (Figure I-1, points 8, 9 and 10)

This stream contains water from rolled powder blender cleaning operations.

In addition to the process water streams, some effluents derive from the use of wet scrubbers. These scrubbers are used to collect dust from grinding, weighing and sieving operations. Since virtually all components of propellants undergo these preparatory operations, these scrubbers are a major source for entry of additives into the environment.

Effluents from washdowns and storm runoff also enter the New River. These effluents may contain substantial amounts of propellant ingredients. Entry of chemicals into the environment from these sources is sporadic and the quantities indeterminate.

There has never been a complete quantitative determination of the amount of additives in the RAAP effluent. An analysis of "water-dry" discharges indicated losses of 1-2 lb/day of diphenylamine and 0.5-1.5 lb/day of dibutyl phthalate (Glennon, 1977). However, other sources exist which were not measured, so the above number may represent as little as 10-20% of the total of the compounds entering the environment from RAAP operations. A complete analysis of the effluents would be useful, but would not determine the effects of "surges" from washdowns or storms.

a. Effluents from Propellant Production

The effluent quantities from propellant processing operations were recorded for the time period 1973-74 (Smith and Dickenson, 1974). These figures are presented in Table I-7.

The following quantities of dissolved solids appear in effluents based upon the figures in Table I-7.

Solvent Process

Operation	Effluent, K gpd	Dissolved Solids in Effluent (lb/day)
Cast Propellants	30.2	223
Single Base, A, B, C lines	86	215
C-line, High Energy	74	383
Solvent Recovery	239	211
Propellant Finishing	230	173
Solvents Rectification	148	1513
	807.2	2718

Solventless Process

Operation	Effluent, K gpd	Dissolved Solids in Effluent (lb/day)
All Operations	167	476

Table 1-7. Effluents from Propellant Processing Operations  
(Smith and Dickenson, 1974).

<u>Operation</u>	<u>Effluent Quantity, gpd</u>	<u>Avg Dissolved Solids, mg/l</u>
<u>Cast Propellant Area</u>		
TOW Machinery	24,000	210
Benite Saw Houses	6,000	3592
Tray Wash	200	669
<u>Single Base Propellant Areas</u>		
A-line, East 1/2	18,000	188
A-line, West 1/2	10,000	113
B-line	28,000	294
C-line	30,000	437
<u>Double and Multibase Propellants</u>		
C-line, High Energy	74,000	620
<u>Solvent Recovery Area</u>		
Water Dry	15,000	152
Sorting	210,000	102
Solvent Recovery	14,000	111
<u>Propellant Finishing Area</u>		
Coat and Glaze	230,000	90
<u>Solventless Propellant Areas</u>		
Blender	45,000	76
Process Buildings, Cleanup	7,200	1582
Process Buildings, Normal Operations	85,000	462
RAP Machines	30,000	96
<u>Solvent Rectification Area</u>		
Chem Mix	17,000	134
Ether Still	66,000	40
Alcohol Rectification	65,000	2716

Production rates from Oct 1973 - Sept 1974 were as follows (Glennon, 1977):

Solvent Process, Single base	75.5 million lb
Solvent Process, Double and Multibase	2.13 million lb
Solventless Process	3.25 million lb

Thus, dissolved solids in effluents from all solvent process operations averaged 1.3% of the amount produced. For the solventless process, dissolved solids in effluents represented 5.3% of the amount produced. For double and multibase propellants only (solvent process), wastes in effluents represented 6.6% of the propellants produced.

Assuming that each additive appeared as dissolved solids in the effluents in proportion to its concentration in the formulation, the following estimates of losses were determined:

<u>Additive</u>	<u>Estimated Losses in Effluents, 1973-1974</u>	
	<u>lb/day</u>	<u>lb/month</u>
Ethyl centralite	20-40	600-1200
Diphenylamine	15-25	450-750
2-nitrodiphenylamine	9-18	270-540
Diethyl phthalate	15-25	450-750
Dibutyl phthalate	40-80	1200-2400
Triacetin	20-50	600-1500
Lead salicylate	5-10	150-300
Lead stearate	1-2	30-60
Lead resorcyate	5-10	150-300
Barium nitrate	1-3	30-90

These losses represent propellant processing operations only. Additional losses from chemical preparation operations are not included.

#### b. Radford AAP Discharges into New River

In 1971, Radford AAP discharged 50 mgd to the New River (Rosenblatt et al., 1973). Of this amount, 3.4 mgd was effluent from single base propellant operations in A-line and B-line. At this time, single base propellant production by the solvent process was at about 30% of capacity, or about 50 million lb/year. The discharge from single base propellant operations was estimated to contain 2,800 lb/day of nitrocellulose (Rosenblatt et al., 1973).

The additives used in single base propellants include ethyl centralite, diphenylamine and dibutyl phthalate. Based upon the estimated discharge of nitrocellulose (2,800 lb/day), the following amounts of these additives would be expected to be present in the effluent.

Ethyl centralite	3-12	lb/day
Diphenylamine	30-35	lb/day
Dibutyl phthalate	90-150	lb/day

The New River carries a mean flow of 2,380 million gallons per day (mgd). The lowest 7-day average flow has been calculated to be 620 mgd, with a frequency of occurrence of once every 10 years (Glennon, 1977). The record low daily flow was recorded to be 320 mgd (Rosenblatt *et al.*, 1973). It is known that at Radford AAP, rapid mixing of discharges with river water does not always occur. Extended mixing zones have been found to occur with localized high concentration of pollutants (Glennon, 1977).

### 5. Current Effluent Treatment

Currently, each process stream is filtered. The propellant particles are collected and burned in an open burning ground. Some waste streams, such as the C-line waste water, are lagooned before discharge to the river. This lagoon provides a holding capacity to minimize the effects of surges in chemical content. Such surges may occur as a result of spills, washdowns, etc.

The propellant particles collected on the filters are essentially insoluble in water. The additives in the propellants are also generally sparingly soluble in water. However, the possibility exists for leaching small quantities of the additives from the propellant particles and thus allowing them to enter the river. Most of the additives are toxic compounds and may be of environmental concern even in small quantities. It has been established that significant reductions in biological life occur in the New River at the RAAP site (Smith and Dickensen, 1974). The effects dissipate rapidly downstream of the plant, however.

### 6. Future Effluent Treatment Plans

RAAP is currently in the process of designing or constructing improved facilities for the treatment of propellant process effluents. The general types of treatment are:

1. Chemical treatment facilities will be installed for removal of inorganic salts.
2. Biological treatment facilities are planned for removal of organic propellant ingredients.
3. Carbon absorption is planned for removal of organics from wastes from solvent process propellant manufacture.
4. Process water will be treated and recycled whenever possible rather than discharged.
5. Liquid wastes will be segregated and each treated according to its individual needs in order to meet effluent standards.

These facilities are being designed on the basis of general waste stream characteristics such as:



- Chemical Oxygen Demand (COD)
- Biological Oxygen Demand (BOD)
- Total Carbon (TC)
- Total Organic Carbon (TOC)
- Total Solids
- Percent Volatiles
- Dissolved Solids
- pH

In general, there have been few analyses of the specific concentration of individual propellant additives. An exception is lead, which is sometimes measured quantitatively in waste streams (Randall and King, 1971). Other additives such as diphenylamine, triacetin, dibutyl phthalate, diethyl phthalate and ethyl centralite have been measured quantitatively in conjunction with pollution abatement studies (Smith and Dickensen, 1972; *ibid*, 1974). However, these or other additives are rarely, if ever, determined in effluents from plant operations.

Studies to characterize treatability of propellant wastes (Randall and King, 1971; Smith and Dickensen, 1972; *ibid*, 1974) have looked into both biological and physical/chemical methods. Some conclusions reached in these studies are noted below:

1. Organic components of waste streams can be degraded by activated sludge in both batch and continuous processes. With a retention time of 12 hours, about 90% reduction of COD and BOD was achieved (Smith and Dickensen, 1972).
2. Physical treatment of C-line waste water resulted in removal of about 2% of the original TOC. The processes used were sedimentation (settling), filtration and air stripping (Randall and King, 1971).
3. Activated sludge treatment of C-line waste water resulted in 70-80% reduction in BOD in 12 hours (Randall and King, 1971).
4. Rolled powder area wastes appear to be toxic to activated sludge and cannot be readily biodegraded (Randall and King, 1971).
5. Inorganic propellant ingredients can be effectively removed from waste waters by reverse osmosis or ion exchange (Smith and Dickensen, 1974).
6. Organic propellant ingredients can be removed from waste water using activated carbon (Smith and Dickensen, 1974).
7. Reverse osmosis is effective for removing higher molecular weight organic propellant ingredients (Smith and Dickensen, 1974).
8. Ozone oxidation will decompose propellant ingredients such as diphenylamine and dibutyl phthalate (Smith and Dickensen, 1974).

9. Lead concentrations can be reduced to about 1 mg/l by chemical precipitation and flocculation (Smith and Dickensen, 1974).

Current plans for effluent treatment at RAAP are based upon guidelines which specify waste quality in terms of BOD, COD, TOC, etc. However, both in biotreatment and physical/chemical treatment, it is likely that some components of the waste will pass through essentially unchanged. These recalcitrant compounds are often the most harmful from an environmental standpoint. Some propellant additives are probably in this category. There are also serious questions concerning possible biotransformation of some constituents to species which are of even more environmental concern than the original compounds.

In addition to the overall reduction of COD and BOD, future effluent guidelines will require the removal of toxic chemicals from the waste streams to below a predetermined limit. Thus, biotreatment with activated sludge or physical/chemical processes which do not degrade all of the propellant additives may be insufficient. A need exists for characterization of propellant waste streams to determine the actual concentrations of potentially harmful additive compounds. The extent to which they will be mitigated in the planned treatment processes should also be determined.

## B. Propellant Loading

### 1. Propellant Loading Processes and Facilities

Propellants are blends of up to twelve additives plus the basic ingredients, nitrocellulose and nitroglycerin (Patterson *et al.*, 1976). The additives include metal powders, oxidizers, stabilizers, modifiers, plasticizers and burning rate catalysts. The propellants are manufactured and processed into shapes ranging from small pellets to cylinders several feet in diameter and six feet or more in length at Radford, Indiana, Badger and Sunflower AAPs. They are shipped from these manufacturing plants to LAP (Load, Assembly and Pack) plants for loading. The LAP operations are accomplished at the following plants:

- Army's Longhorn AAP in Marshall, Texas
- Army's Redstone Arsenal in Huntsville, Alabama
- Navy's NOS Indianhead in Crane, Indiana
- Navy's NIROP Magna AAP in Magna, Utah
- Air Force Plant 78 in Brigham City, Utah

#### a. Propellant Pallet Loading

Propellant pellets are also referred to as ball powder. They are often loaded as is for gun propellants. In this process, cartridge cases are fed into an assembly machine and filled by automatic loaders. The projectile is sealed into the head of the cartridges, which are then boxed for shipment.

Loading lines are relatively small operations requiring only 2-3 personnel to function. The quantity of propellant permissible each line is in the range of several hundreds of pounds. The personnel and propellant limitations are intended to minimize the effect of incidents involving the propellants by restricting damage to a relatively small area.

b. Rocket Motor Grain Loading

Most double base propellants are formed into grains by hot extrusions through dies. These grains are cut to the desired length, then dried and cured. They are then machined to the exact final dimensions required for their use. The outer surfaces and ends are usually coated with a combustion inhibitor to restrict burning to the inside surface. At motor assembly plants, the grains are simply inserted into the motor cases. Larger grains may be cemented in place. Smaller grains are more often simply slipped in like batteries in a flashlight.

c. Cast-in-Place Rocket Motor Loading

There are two basic types of cast-in-place rocket motor grains. These are referred to as "plastisol" and "polymerization cured" grains. Plastisol grains involve high energy propellant compositions and are used in advanced solid motors such as required for ICBM's. In the casting operation, a casting powder is poured into the rocket motor case from the nozzle end. The case is vibrated to increase the propellant bulk density. Air is evacuated and a liquid nitroglycerin mixture is poured in to fill the voids. A mandrel in the center of the motor cavity is used to form a star-shaped pattern in the grain.

Once loaded, the motor is placed in a 40°C oven for several days. During this time, the liquid forms a uniform rubbery gel with the casting powder. After curing is complete, the motor is cooled and the mandrel removed. The grain end is then coated with a burning restrictor and the nozzle and ignition hardware installed.

In contrast to plastisol grains, the propellant ingredients and the oxidizer of polymerization grains are pre-mixed before insertion into the motor. The fuel components including additives are mixed with a liquid monomer to form a thin slurry. The oxidizer, generally ammonium perchlorate, is ground separately to a fine powder, then transported to the final mixing area.

The fuel slurry and the oxidizer powder are mixed by slow addition of the oxidizer. Several thousand gallons are mixed at one time. All mixing is accomplished by remote control. When the mixture is uniform, the polymer cross-linking agent is added. The mixing apparatus is then transported to the casting site and positioned over the empty motor case. The propellant, in the form of a thick slurry, flows into the case. When filled, the motor is heated to cure the propellant as with the plasticol type.

## 2. Waste Streams

LAP operations do not generate as much waste water as manufacturing operations, primarily because there is no process water used in loading. The major source of waste streams is from floor washdown operations. The constituents of waste streams from loading operations include:

- propellant particles and dust
- dissolved propellant ingredients including additives
- metal particles and solvents from cleaning and painting operations

Another source of wastewater in some LAP facilities is air pollution control scrubber water (Patterson *et al.*, 1976). Dust and particulates collected in wet scrubbers contaminate the water. Thus, discharges from air scrubbers may contain significant quantities of propellant ingredients, both dissolved and in solid form.

At Longhorn AAP, most wastewaters are generated by clean-up operations (USAEHA, 1972). The only major exception to this generalization is the M-120 Area in which the mixing, processing and loading of propellants for rocket motors takes place (USAEHA, 1972). The other areas are used primarily for assembly operations.

## 3. Current Effluent Treatment at Longhorn AAP

Wastewater from the processing and loading operations at Longhorn AAP are collected in sumps. These sumps are pumped out on a regular basis and the contents transported to an evaporation pond located near the open burning area.

There is no segregation of waste streams or any pre-treatment before discharge into the pond. The pond is heavily contaminated with both solid and dissolved propellant ingredients. Definite biologic stress has been noted in the pond (Fox *et al.*, 1975).

The sumps which provide the input material to the pond are carefully watched to see that they are emptied before overflow occurs. There are about 80 sumps, however, and overflow has occurred in some cases. These incidents have not resulted in any measureable contamination of surface waters (USAEHA, 1970).

Of greater concern is the evaporation pond itself. The surface of the pond covers about 2 acres. The pond has never been known to overflow. In the past, motor case cleanout operations at the pond site nearly filled it, so these operations were stopped. Heavy precipitation has occurred, but never enough to overflow the pond. However, LAAP is currently operating at only about 10% of capacity. If full mobilization were to occur, the pond would not be an adequate sink for wastewaters.

The pond loses water by evaporation and percolation into the soil. It is estimated that about 6-8 inches of propellants are present in a layer on the pond bottom. Thus, water percolating into the soil contains any soluble additives leached from the propellants. No ground water contamination appears to have occurred from this pond (USAEHA, 1972). However, it is also possible that no ground water contamination was noted because specific propellant additive compounds were not monitored.

Some propellant LAP plants, namely Air Force Plant #78 and Redstone Arsenal, have installed dry collection systems for air cleaning. Thus, the generation of air pollution control scrubber water is eliminated. Any particulates are removed and disposed of by burning. Such systems have been found to be effective and should be considered for other plants (Patterson *et al.*, 1976).

#### 4. Future Effluent Treatment Plans

Longhorn AAP is planning the construction of a new evaporation pond. This new pond would either supplement or replace the current pond. At some future time, the current pond may be drained so that the propellant layer can be recovered and destroyed.

In many plants, treatment and recycle of water is planned. Filtration of solids from wastewaters will allow them to be recovered for disposal by burning. Other constituents may be precipitated by chemical treatment, thus improving the water for at least partial reuse. There appears to be no plans for segregation of solids from liquids in the sumps at LAAP. Thus, propellant additives will continue to be discharged into the evaporation pond or ponds. The environmental impact of this action needs to be further assessed.

#### C. Disposal of Solid Propellant Wastes

##### 1. Waste from Propellant Manufacturing

###### a. Current Disposal Methodology

Wastes from propellant manufacturing operations at Radford AAP include the following:

- Solids collected from process water filters
- Particulates from chemical preparation steps collected in wet or dry air scrubbers
- Dust from additive or propellant handling operations
- Solids filtered from water used for washdowns
- Scraps from grain machining operations

These materials are collected and transported daily to the open burning ground. The burning ground is a 20 acre area located in the "Horseshoe" of the New River (Figure I-1, point 17). This area is used each day to burn floor sweepings,

off-specification batches of propellants or explosives, and the particulates from the effluent filters (Bender *et al.*, 1975).

#### b. Future Disposal Plans

In the future, virtually all solid wastes from propellant manufacture will be incinerated under carefully controlled conditions rather than burned in open areas. At Radford AAP, two incinerators will be used. One will be specifically for waste explosives or propellants. The other will handle materials such as wood or paper which have been contaminated with small amounts of high-energy materials.

##### Contaminated Waste Incinerator

The contaminated waste incinerator is currently operational at RAAP. This unit is an "air curtain" incinerator. The materials to be burned are placed upon a grating. An air curtain surrounds the grating, and air also circulates under the grating to promote complete combustion. This incinerator is essentially an open burning system. However, the forced air circulation promotes complete combustion and helps contain combusting materials in the burning zone.

##### Explosive Waste Incinerator

The explosive waste incinerator was constructed and completed in 1977. However, it does not meet performance specifications and requires modification. These modifications are expected to be underway in early 1978. The incinerator should come on stream in late 1978 or early 1979.

The incinerator is a rotary kiln type with a barrel about 10 ft. long. Waste propellants are ground and slurried with water. They then fed into the kiln countercurrent to an oil fired flame. This system will permit complete and controlled destruction of the explosive materials.

#### 2. Wastes from Loading Operations

Propellant wastes from loading operations are generally limited to solid particles which are spilled at loading sites. As an example, in the loading of ball powder into cartridges, a cartridge will occasionally overturn, dumping the contents on or near the loading equipment.

Solid wastes of this type are generally collected dry and transported to a burning site. Dust or residuals are collected in washdown operations, generally at the end of each shift. In some cases, solids are segregated and burned. In others, they are discharged with the water.

#### 3. Outdated Propellants

Munitions which are out of specification, or have exceeded their maximum shelf life, must be disposed of. Also rocket motor cases are sometimes cleared out for reuse if the original propellant loading was unsatis-

factory. These operations may generate a substantial amount of waste propellant.

a. Current Disposal Methodology

Cartridges or small rocket motors may be emptied easily by dumping. The propellants thus collected are merely transported to burning sites for disposal.

Larger motors in which the propellant is cemented in or cast in place require more complex removal methods. The propellant may be machined out, or removed hydraulically or with steam. These processes generally leave residual propellants in the cases. These are removed by solvents or by water washing.

Washing out large motor cases generates large amounts of contaminated wastewater. At Longhorn AAP, motor cases cleaning operations were causing the evaporation pond to be overfilled. Consequently, motor cleaning is no longer accomplished at the pond site.

b. Future Disposal Plans

As with other sources of propellant waste, outdated propellants will be incinerated in the future rather than burned in open pits. Contaminated wastewaters will be segregated for filtration and other physical or chemical treatment as required.

A new Army demilitarization facility is under construction at Hawthorne, Nevada. This facility is scheduled to be operational in 1980 and will be the primary location for demilitarization and disposal of waste or outdated munitions. Only munition and items which have been sent to the field will be treated at Hawthorne. The individual AAP's will still have the responsibility for disposal of wastes generated from their own operations.

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AD

**PRELIMINARY PROBLEM DEFINITION STUDY OF  
48 MUNITIONS-RELATED CHEMICALS**

**VOLUME II PROPELLANT RELATED CHEMICALS**

**ETHYL CENTRALITE**

**FINAL REPORT**

**J. F. Kitchens  
W. E. Harvard III  
D. M. Lauter  
R. S. Wentzel  
R. S. Valentine**

**April 1978**

**Supported by:**

**U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND  
Fort Detrick, Frederick, Maryland 21701**

**Contract No. DAMD17-77-C-7057**

**COTR: Clarence Wade, Ph.D.**

**ATLANTIC RESEARCH CORPORATION  
Alexandria, Virginia 22314**

**Approved for Public Release  
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**The findings in this report are not to be construed as an  
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### SUMMARY

Ethyl centralite is a urea derivative used exclusively in the United States as a stabilizer in solid propellant formulations. The stabilizing action of ethyl centralite is through its reaction with nitrites and nitrates formed by the decomposition of the propellant primary explosives, i.e. nitrocellulose, nitroglycerin and nitroguanidine. Percentage of ethyl centralite in the propellant formulations range from 0.02% to 6.5%. Ethyl centralite is used at all four of the Army's propellant manufacturing plants when they are in operation. These plants are Radford, Badger, Sunflower and Indiana AAP. Currently only Radford and Indiana AAPs are operational. Current consumption of ethyl centralite at Radford AAP is 31,000 lb/month. At full mobilization 150,000 lb/month would be used by Radford AAP alone. Ethyl centralite enters the environment from the preparation operations, building washdown and in process water from the solvent process propellant production. Current Radford AAP discharges to the New River are estimated at 300 to 530 lb/month. At full mobilization discharges up to 2500 lb/month could occur.

At the present time, there are no producers of ethyl centralite in the United States. There is one manufacturing facility for ethyl centralite in the United States, however, it is currently not operational. The supplies of ethyl centralite are obtained from French or German sources.

Only one mammalian toxicity study on ethyl centralite was uncovered during this preliminary overview. These researchers found an intraperitoneal LD50 of 200 mg/kg for mice. In an aquatic toxicity study with salmon, ethyl centralite was shown to be extremely toxic to aquatic life.

Thus, ethyl centralite is a compound that is unique to propellant manufacturing. Since the military is one of the main formulators of propellants, ethyl centralite can be considered a military unique chemical. Therefore, the following studies are recommended to further evaluate the toxicological and environmental hazards of ethyl centralite:

- a Phase II detailed literature evaluation
- analysis of sediment sample
- aquatic toxicity studies if the literature evaluation reveals the need for more information

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## FOREWORD

This report details the results of a preliminary problem definition study on ethyl centralite. The purpose of this study was to assess the Army's responsibility for conducting further research on ethyl centralite in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on ethyl centralite, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Ethyl centralite was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized during this study.

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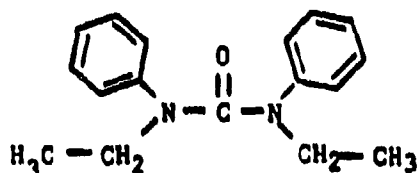
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## II. ETHYL CENTRALITE

### A. Alternate Names

Ethyl centralite is a urea derivative possessing the following structure:



It has a molecular formula of  $C_{17}H_{20}N_2O$  and a corresponding molecular weight of 268.36 g/mole. Alternate names for ethyl centralite are listed below:

CAS Registry No.	85-98-3
CA Name (9 CI):	Urea, N,N'-diethyl-N,N'-diphenyl-
CA Name (8 CI):	Carbanilide, N,N'-diethyl-
Wiswesser Line Notation:	2NR&VN2&R
Synonyms:	Carbamite, Centralite, Centralite 1; 1,3-diethyl-1,3-diphenylurea; Ethyl centralite; N,N'-diethyl-N,N'-diphenylurea; N,N'-diethylcarbanilide; Sym-diethyl- diphenylurea.

### B. Physical Properties

The physical properties of ethyl centralite are presented in Table II-1. The infrared spectrum of ethyl centralite shows absorptions at 3050, 2980, 2940, 1660, 1600, 1500, 1450, 1390, 1370, 1290, 1270, 1130, 1080, 1070, 750, and 690  $cm^{-1}$  (CRC, 1974). The ultraviolet spectrum of ethyl centralite in methanol shows an absorption maxima at 245 m $\mu$  (CRC, 1974).

### C. Chemical Properties

#### 1. General Reactions

Nitrosation and nitration studies on ethyl centralite have been conducted to examine its role as a propellant stabilizer (Taymaz *et al.*, 1977; Roy, 1968). Nitrosation was performed using nitrous acid ( $HNO_2$ ) in hydrochloric acid (HCl). The amounts of nitrous acid employed ranged from 2 to 50 molar equivalents of ethyl centralite.

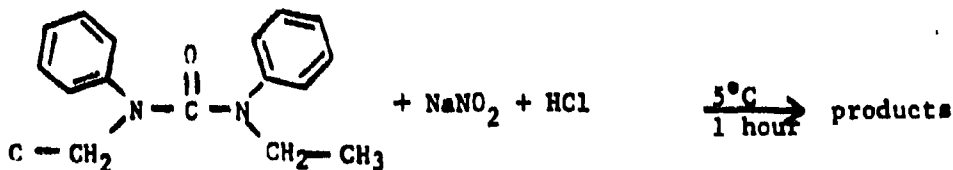


TABLE II-1. Physical Properties of Ethyl Centralite\*.

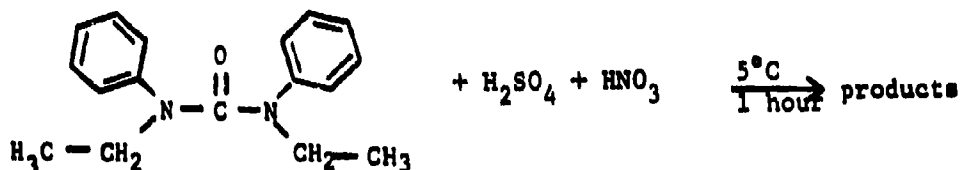
Physical Form @ 20°C:	Crystalline solid
Color:	White
Odor:	Peppery
M.P.:	79°C
B.P.:	325-300°C
Specific Gravity:	1.12 @ 20°C
Solubility:	Water - insoluble Soluble in most organic solvents.

\*References: Windholz, 1976; Sax, 1976; Hawley, 1977.



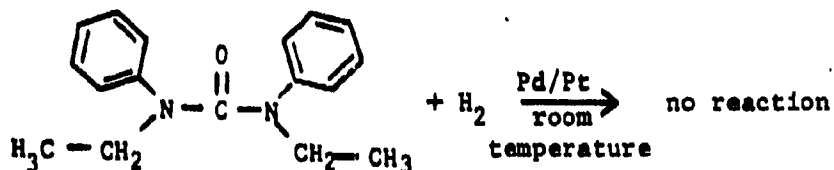
The major products were various nitro derivatives of ethyl centralite. When concentrations greater than 8 equivalents of nitrous acid were used, nitro-N-ethylanilines and trinitrobenzene appeared in the product mixture. It was necessary to raise the concentration of  $\text{HNO}_2$  to 50 molar equivalents before unreacted ethyl centralite was not found in the products. At this high concentration, traces of nitro-anilines were formed.

Ethyl centralite was nitrated by the action of a standard mixture of sulfuric and nitric acids at  $5^\circ\text{C}$  for 1 hour.



The amount of nitric acid used ranged from 1 to 112 molar equivalents relative to ethyl centralite. Minimal reaction was observed using 1 molar equivalent of  $\text{HNO}_3$ . Higher concentrations of nitric acid yielded numerous nitro derivatives, nitro-N-ethylanilines, nitroanilines, and miscellaneous nitro aromatics.

Roy (1960) also attempted to hydrogenate ethyl centralite. He treated it with  $\text{H}_2$  at 20 psi and Pt black and Pd black catalysts. No reaction was observed.



## 2. Environmental Reactions

Ethyl centralite is stable in water. Its resistance to hydrolysis has been attributed to the bulkiness of the ethyl and phenyl substituents. Hydrolysis involves initial nucleophilic attack by hydroxide anion (or by a molecule of water in acid). The mechanism in acid requires prior protonation of carbonyl oxygen, enhancing its electrophilic character. The carbonyl reforms as N-ethylaniline is lost. The N-substituted carbamic acid spontaneously decarboxylates forming a second N-ethylaniline and  $\text{CO}_2$ . The hydrolysis is shown schematically in Figure II-1.

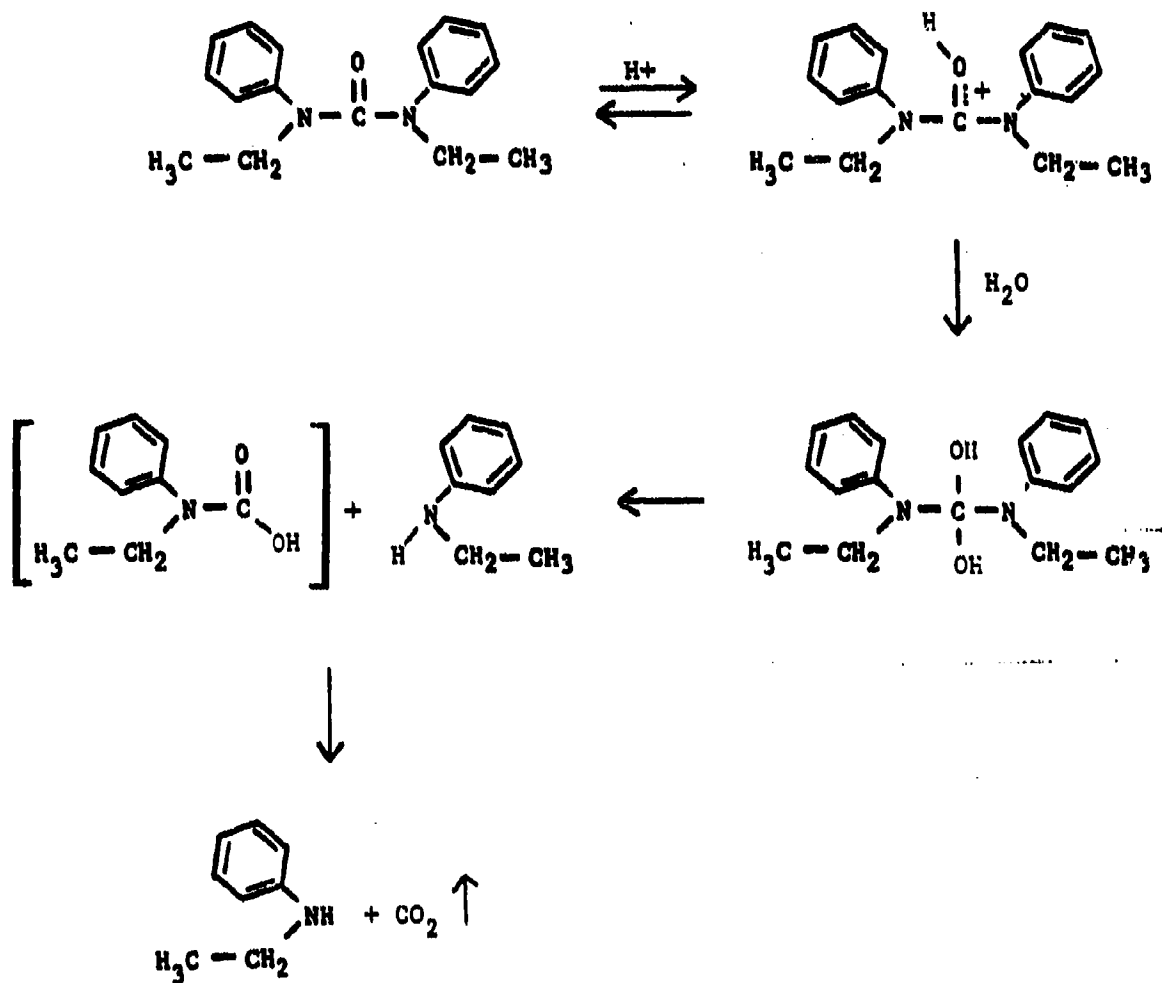


Figure II-1. Acid Hydrolysis of Ethyl Centralite

Hydrolysis has been observed in strong sulfuric acid. Following reflux of ethyl centralite for three hours in 30% H<sub>2</sub>SO<sub>4</sub>, 94% of the starting material was recovered. None of the expected hydrolysis product was found. Refluxing for four hours in 40% H<sub>2</sub>SO<sub>4</sub> yielded tar formation and traces of N-ethylaniline. Complete hydrolysis was achieved by refluxing ethyl centralite for three hours in 60% H<sub>2</sub>SO<sub>4</sub>. Seventy-one percent of the theoretical N-ethylaniline was recovered with tar formation accounting for the remaining material.

Even under severe conditions, ethyl centralite resists base catalyzed hydrolysis. Ninety percent of the starting material was recovered following four hours of refluxing in 50% aqueous NaOH. Minor amounts of tars formed.

### 3. Sampling and Analysis

Two-dimensional thin layer chromatography can be employed for the isolation of ethyl centralite. It has been used in the examination of the products of reactions of centralite (Roy, 1968; Taymaz *et al.*, 1977) and in the determination of centralite and derivatives in artificially aged propellants (Roy, 1968). Separation was achieved on glass plates coated with silica gel with a two developer (solvent) system. The sample was first chromatographed using ethylene dichloride and then chromatographed at right angles with a 75:25 petroleum ether:ethyl acetate solution.

Ethyl centralite may also be identified by its absorption spectrum ( $\lambda_{\text{max}}$  - 247 nm). However, the presence of N-ethylaniline ( $\lambda_{\text{max}}$  - 247 nm) will interfere with this determination.

### D. Uses in Army Munitions

#### 1. Purposes

Ethyl centralite is used as a stabilizer for numerous propellant formulations as shown in Table II-2. These formulations include single, double and multibase propellants made by both solvent and solventless processes. Ethyl centralite is used at all facilities which manufacture propellants, including Badger AAP, Sunflower AAP, Radford AAP and Indiana AAP.

#### 2. Quantities Used

##### a. Historical Use

The average amount of ethyl centralite used at Radford AAP during the period 1968-1977 was 343,200 lb annually. The major use was in double and multi-base propellants, which account for 87 percent of the ethyl centralite used. Most of the remainder was used in the single base propellant, BS-NACO. About 1 percent was used to make the M-8 formulation, which is a solventless process, double base propellant. The specific amounts of ethyl centralite procured by RAAP during the period 1968-1977 are given below (Watts, 1978).

Table II-2. Propellants Having Ethyl Centralite As an Ingredient  
(Hercules, Inc., 1977)

<u>Formulation</u>	<u>% Ethyl Centralite in Formulation</u>
Benite	$0.5 \pm 0.1$
BS - NACO	$1.2 \pm 0.2$
HES 6706-1	0.8
M-7	0.9
M-7 for TOW	0.8
M-26	$6.0 \pm 0.5$
M-26E1	$6.0 \pm 0.5$
PNJ Casting Powder	0.02
M-8	$0.6 \pm 0.2$
M-30	$1.5 \pm 0.1$
M-30A1	$1.5 \pm 0.1$
M-30A2	$1.5 \pm 0.1$
PNJ for TOW	0.02
Bermite	2.0
MR-23 adhesive	$0.3 \pm 0.1$

<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
511,175	695,950	140,350	233,430	444,325	60,725	399,469	356,650	285,268	304,649

b. Current Use

During 1977, Radford AAP used ethyl centralite at an average rate of 31,200 lb/month. Based upon December, 1977, production of propellants, the following amounts of ethyl centralite were used in December, 1977, alone:

<u>Propellant</u>	<u>Lb. Produced December, 1977</u>	<u>Lb. Ethyl Centralite Used</u>
Bermite	25,000	125
M-7	6,000	54
M-26	242,000	14,520
M-8	32,000	192
M-30	683,000	10,245
M-30A2	453,000	<u>6,795</u>
		31,931

Thus, December, 1977, was a typical month with respect to use of ethyl centralite with about 102% of the average monthly amount consumed.

c. Use at Full Mobilization

Not all of the propellants specifying ethyl centralite in their formulations could be produced at the same time, as they use common facilities. It is estimated, however, that full mobilization operations at Radford AAP would consume about 150,000 lb/month of ethyl centralite.

3. Documented or Speculated Occurrences in Air or Water

The actual concentrations of ethyl centralite in waste streams have not been measured. Effluents containing ethyl centralite would be expected to be generated from the following sources:

- Preparation operations including weighing, grinding, or classification. Dust or particulates are collected in wet scrubbers from which both solid wastes and contaminated effluents may be generated.
- Residues from washdown operations generate effluents which are filtered and discharged. Collected solids are transported to the burning grounds.

- Process water from the manufacture of propellants by the solvent process. These effluents appear in the C-line waste water stream, the 48-inch general purpose sewer, and the solvent recovery area discharges.
- Process wastes from solventless propellant manufacture. These effluents appear in the rolled powder area waste streams.

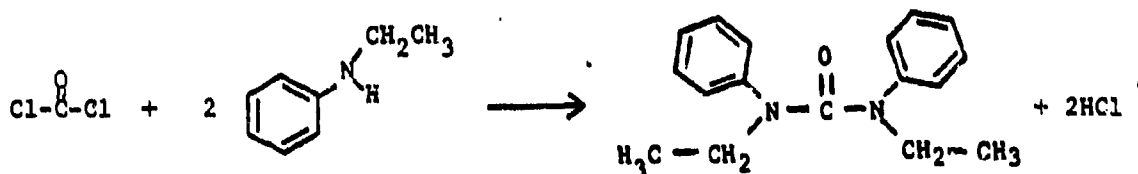
It is estimated that 1-2% of the propellants produced are lost during processing operations. Another 2-3% of the ethyl centralite handled may be lost during preparation operations (Dickenson, 1978). Thus, total amount of ethyl centralite in waste streams amounts to 900-1600 lb/month, based upon current production rates at Radford AAP. Full mobilization losses would range from 4,500 to 7,500 lb/month.

Ethyl centralite is sparingly soluble in water. Much of the material lost is collected in solid form on effluent stream filters. This material may be collected and burned, thus never reaching the New River. However, depending upon the frequency of particulate removal from the filters, some ethyl centralite may leach out of the collected solids. It is estimated that 1/3 of the total ethyl centralite loss may ultimately appear in effluents reaching the New River.

#### E. Uses in the Civilian Community

##### 1. Production Methodology

Ethylcentralite is made by the reaction of phosgene with two equivalents of N-ethylaniline.



The reaction is run in the absence of water and HCl is removed as a gas (Cordova Chemical, 1977).

##### 2. Manufacturers, Production and Capacity

In the recent past, Story Chemical Company was the only U.S. manufacturer of ethyl centralite. Story was recently purchased by the Cordova Chemical Company, who has currently shut down all plant operations. No decision has been made as to whether or not Cordova will resume the production of ethyl centralite (Cordova Chemical, 1977). Former production and capacity statistics are unavailable.

### 3. Usages

There are no non-propellant related uses of ethyl centralite.

### 4. Future Trends

No new civilian uses for ethyl centralite are anticipated.

### 5. Documented or Speculated Occurrences in the Environment

No occurrences of ethyl centralite in the environment from civilian manufacture have been recorded in the literature.

## F. Comparison of Military and Civilian Usage and Pollution

The only major use of ethyl centralite in the United States is as a stabilizer in propellants. There are no U.S. civilian producers which currently manufacture ethyl centralite. The Army purchases all of its ethyl centralite from French or German sources through the following importers:

- Wallach-Gracer Export Corporation
- Kingsley and Keith

Thus, the Army is the major user and polluter of ethyl centralite.

## G. Toxicological and Environmental Hazards

### 1. Toxicity to Mammals

Little research has been conducted on the toxicity of ethyl centralite. Doull *et al.* (1962) studied the toxicity of ethyl centralite to mice. They found the intraperitoneal LD50 for ethyl centralite to be 200 mg/kg. This result would indicate that ethyl centralite is a fairly toxic substance. It is also known that ethyl centralite can be absorbed through the skin. A need for further investigation into the mammalian toxicity of ethyl centralite is indicated by this limited study.

### 2. Aquatic Toxicity

The distribution of ethyl centralite in the aquatic environment has not been studied. MacPhee and Ruelle (1969) found that when the Northern Squawfish (*Ptychocheilus oregonensis*), Chinook Salmon (*Oncorhynchus tshawytscha*), and Coho Salmon (*O. kisutch*) were exposed to 10 ppm of ethyl centralite, they died within one to three hours.

Based upon the estimated losses of ethyl centralite at RAAP, a typical concentration of this material in the New River would be from 1 - 20 ppb. However, at full mobilization, it appears that ethyl centralite would be a toxic hazard to aquatic organisms in the New River. Also, much of the

ethyl centralite released into the effluent is due to washdown, which would produce a surge in the levels of ethyl centralite in New River and increase the toxicity. Eventually, due to ethyl centralite's insolubility, most of the compound will be found in the sediment. Data on the accumulation or bioconcentration of ethyl centralite in aquatic systems is not available. A likely degradation pathway could be the hydrolysis of ethyl centralite to form N-ethylaniline. The impact of N-ethylaniline on aquatic organisms and aquatic systems has not been studied.

### 3. Toxicity to Invertebrates, Microorganisms and Plants

No information was encountered on the toxicity of ethyl centralite to invertebrates, microorganisms or plants.

### 4. Availability of Literature for Phase II

Only two toxicological studies were found on ethyl centralite during this preliminary overview. Sufficient information for a Phase II detailed evaluation of the environment and toxicological hazards of ethyl centralite should be available from the foreign literature, manufacturers and by comparison to closely related compounds.

## H. Regulations and Standards

There are no United States effluent or industrial hygiene standards for ethyl centralite. This compound is not listed in the "EPA Toxic Substances Control Act Candidate List of Chemical Substances."

## I. Conclusions and Recommendations

The goal of this preliminary problem definition study was to evaluate the Army's responsibility for conducting further studies on ethyl centralite. From the information presented in this report the following conclusions can be drawn:

1. Ethyl centralite is a military unique compound. It is not currently manufactured in the United States. The only reported use of this compound is as a stabilizer in solid propellant formulations.

2. Amounts up to 2500 lb/month of ethyl centralite could be discharged from Radford AAP into the New River at full mobilization.

3. Due to its low solubility in water, most of the ethyl centralite will accumulate in the sediment. It may also bioaccumulate in aquatic organisms.

4. The limited toxicological literature evaluated during this study indicates ethyl centralite is highly toxic to aquatic organisms and moderately toxic to mammals.



As a result of this preliminary problem definition study, it is concluded that further research on ethyl centralite should be the Army's responsibility. It is therefore recommended that the following studies be undertaken

- A Phase II detailed evaluation of the toxicological and environmental hazards of ethyl centralite should be initiated.

- Sampling of sediments near the Ramford AAP outfalls should be undertaken to evaluate the accumulation of ethyl centralite.

- Depending on the findings in the Phase II literature evaluation, additional aquatic toxicological studies should be undertaken. Bioaccumulation factors should also be evaluated during this study.

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PRELIMINARY PROBLEM DEFINITION STUDY OF  
48 MUNITIONS-RELATED CHEMICALS

VOLUME II PROPELLANT RELATED CHEMICALS

DIPHENYLAMINE

FINAL REPORT

J. F. Kitchens  
W. E. Harward III  
D. M. Lauter  
R. S. Wentzel  
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND  
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION  
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Approved for Public Release  
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## SUMMARY

Diphenylamine is used in single base solid propellant formulations produced by the solvent process at Radford, Sunflower, Badger and Indiana Army Ammunition Plants (AAP). It is present in the propellants in amounts ranging from 0.5 to 1.7%. In the propellants, diphenylamine acts as a stabilizer by reacting with NO and NO<sub>2</sub> formed from the degradation of the nitrate ester primary explosives. Current use of diphenylamine at Radford AAP is 120,000 lb/year. At full mobilization, 1,284,000 lb/year of diphenylamine would be formulated into propellants at Radford AAP. Estimated discharges of diphenylamine into the New River are between 1600 and 2650 lb/month at full mobilization. If all four propellant plants were utilizing this chemical at approximately the same full mobilization rate, the Army would need 5,136 million lb of diphenylamine per year.

Diphenylamine is used in the civilian community as an intermediate for a variety of dyes and as an antioxidant for rubber. In 1974 civilian production of this compound was 39.9 million lb/year. This production rate will increase as the dye and rubber market grows and as planned new diphenylamine production facilities become operational.

Diphenylamine is moderately toxic to mammals in acute doses. The major problem of chronic exposure to this chemical is the presence of 4-amino-biphenyl as an impurity. The presence of this carcinogen has overshadowed some of the results of chronic exposure studies with diphenylamine.

Diphenylamine is highly toxic to aquatic organisms with 48 hour LC50 ranging from 0.35 to 3.2 ppm. Microorganisms are able to produce nitrosamine from nitrate and diphenylamine. These compounds can be further degraded. However, their effect on the environment has not been resolved.

Diphenylamine is not a military unique chemical. The current Army use rate of this chemical is only 0.02% of the 1974 civilian production. At full mobilization, the Army's needs could increase to 13% of the 1974 production. Sufficient information is not available to assess the civilian pollution of this chemical. The pollution of this chemical resulting from current propellant manufacture at Radford AAP is estimated at 1800 to 3000 lb/year. This discharge is probably ~5% of that from civilian production and use. Therefore, the Army's responsibility for further research on this chemical is questionable. However, due to the high aquatic toxicity of diphenylamine, very low levels (12 ppb) have been suggested for protection of aquatic organisms. If this suggested level is adopted, the Army may not be able to meet the effluent standard. Therefore, it is recommended that the following studies be undertaken

- Sampling and analysis at Radford be performed to determine the quantity of the compound entering the New River
- A literature evaluation of the fate of this chemical in the ecosystem and in proposed treatment facilities

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- Depending on the results of the literature evaluation,  
experimental studies on the fate of this compound may be necessary.

## FOREWORD

This report details the results of a preliminary problem definition study on diphenylamine. The purpose of this study was to determine the Army's responsibility for conducting further research on diphenylamine in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on diphenylamine, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Diphenylamine was only one of the 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized in this study.

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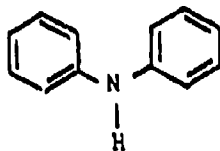
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### III. DIPHENYLAMINE

#### A. Alternate Names

Diphenylamine is an ammonia derivative having the following structure:



The molecular formula of diphenylamine is  $C_{12}H_{11}N$  corresponding to a molecular weight of 169.22g/mole. Alternate names for diphenylamine are presented below:

CAS Registry No.:	122-39-4
Replaces CAS Registry No.:	16044-89-6
CA Name (9CI):	Benzenamine, N-phenyl-
CA Name (8CI):	Diphenylamine
Wiswesser Line Notation:	RMR
Synonyms:	Anilinobenzene; Biphenylamine; DFA; DPA; N-phenylaniline; (Phenylamino)benzene

#### B. Physical Properties

The physical properties of diphenylamine are presented in Table III-1. The infrared spectrum of diphenylamine is presented in Figure III-1.

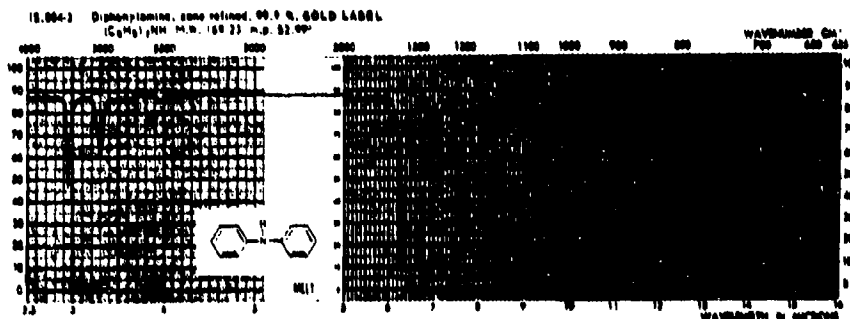


Figure III-1. Infrared Spectrum of Diphenylamine  
(Pouchert, 1970).

The ultraviolet spectrum of diphenylamine shows an absorption maximum at 282 mμ. (CRC, 1974).

Table III-1. Physical Properties of Diphenylamine\*.

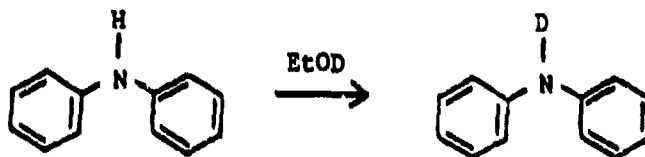
Physical Form @ 20°C:	solid leaflets
Color:	colorless to grayish; darken on exposure to light
Odor:	floral
M.P.:	52.85°C
B.P.:	302°C @ 760 mm Hg 179°C @ 22 mm Hg 168.5-70 @ 14 mm Hg
Specific Gravity:	1.159
Flash Point:	153°C
Autoignition Temperature:	635°C
Solubility:	water - 0.0018g/100g @ 10°C 0.0023g/100g @ 15°C 0.0029g/100g @ 20°C 0.0036g/100g @ 25°C 0.0044g/100g @ 30°C acetone - 70.57g/100g @ 0°C 74.91g/100g @ 28°C methanol - 21.08g/100g @ 0°C 55.15g/100g @ 28°C ethanol - 35.9g/100g @ 19.5°C ethyl ether - 76.45g/100g @ 28°C chloroform - 67.35g/100g @ 28°C benzene - 73.54g/100g @ 28°C

\*References: Windholz, 1976; International Technical Information Institute; Seidell, 1928.

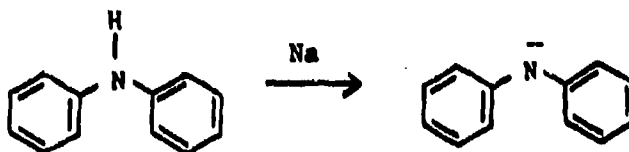
## C. Chemical Properties

### 1. General Reactions

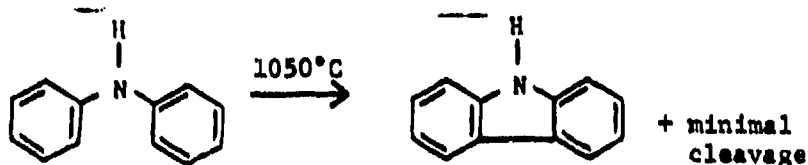
Two aromatic substituents significantly alter the chemistry of diphenylamine from aliphatic amines. Diphenylamine is an extremely weak base and the amine proton is remarkably labile. It is exchanged immediately for a heavy proton in deuterated solvents.



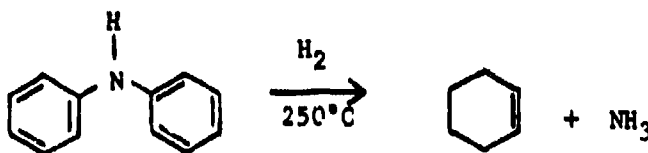
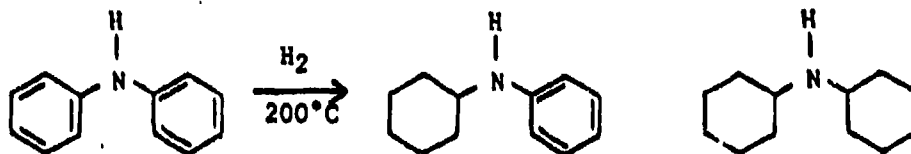
Anhydrous treatment with alkali metal can even remove the proton (Kirk and Othmer, 1964b).



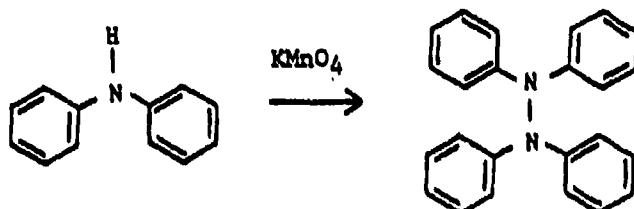
The C-N bonds possess a significant amount of double bond character, making them stronger than normal single bonds. Pyrolysis at 1050°C results in minimal cleavage. The major product is carbazole (Bruzel and Schmeltz, 1971).



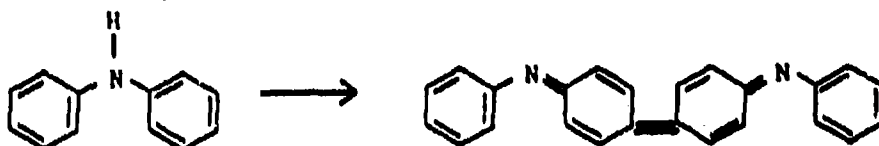
Catalytic reduction at 200°C gives a mixture of N-cyclohexylamine and dicyclohexylamine. At 250°C, reduction occurs with cleavage.



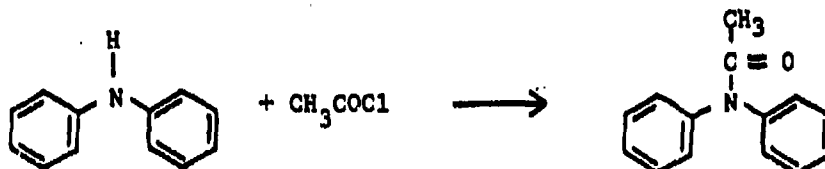
Treatment of diphenylamine with potassium permanganate or several other oxidizing agents yields tetraphenylhydrazine (Kirk and Othmer, 1964b).



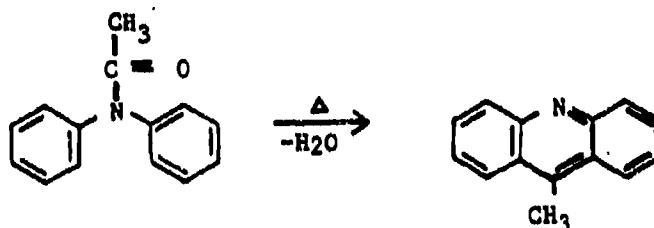
Treatment with milder reagents results in oxidative coupling through the aromatic rings.



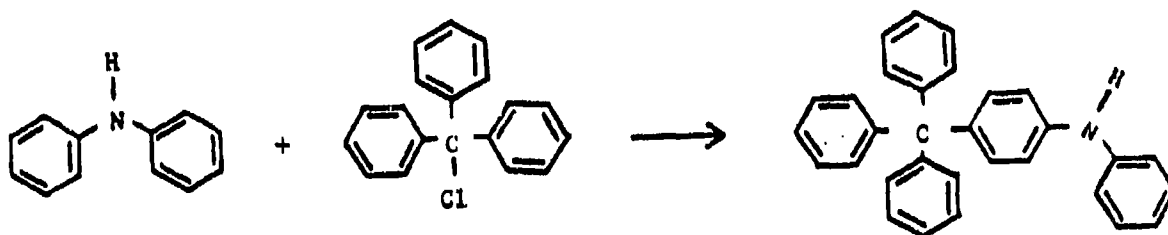
Diphenylamine, like other amines, can behave as a nitrogen nucleophile. It reacts readily with organic acid chlorides and anhydrides to yield N,N-diphenylamides (Kirk and Othmer, 1964b).



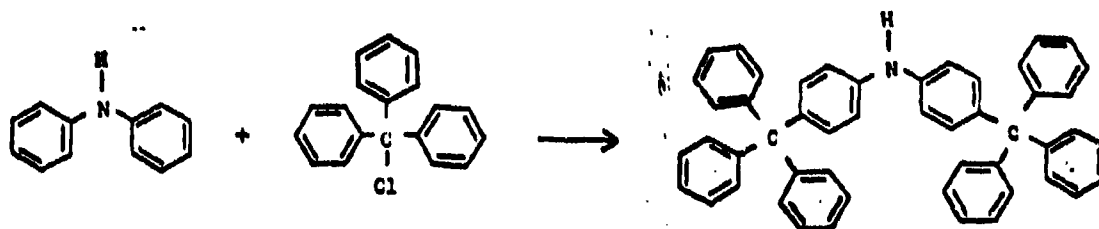
When heated in the presence of dehydrating agents, these amides are transformed to acridine derivatives (Kirk and Othmer, 1964b).



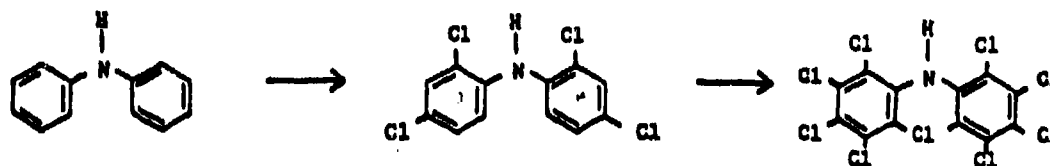
The nitrogen nucleophilic activity of diphenylamine is limited by the bulkiness of the phenyl substituents. In situations where steric considerations are important, the nucleophilic sites on the aromatic rings are more reactive. In the reaction of triphenylmethyl chloride with diphenylamine the para position of the phenyl ring, not the amine hydrogen, behaves as the nucleophile (Kirk and Othmer, 1964b).



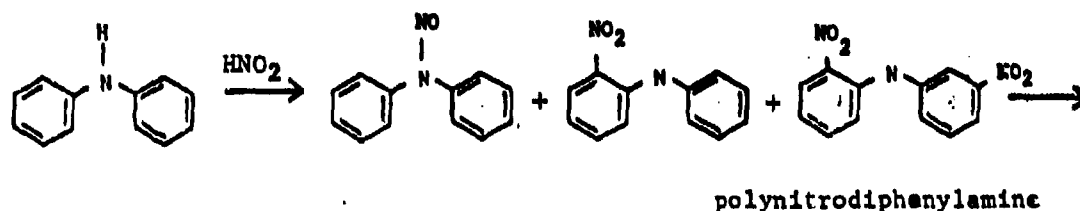
If excess triphenylmethylchloride is present, the reaction will continue.



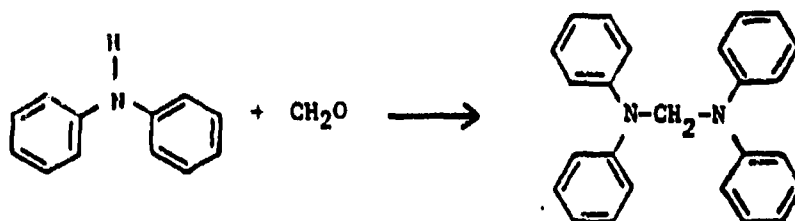
The aromatic rings of diphenylamine are more susceptible to electrophilic substitution than benzene. Halogenation occurs readily and is difficult to stop at the mono- or di- substituted product. The tetra-substituted product is isolatable and the reaction may be driven to yield perchlorodiphenylamine.



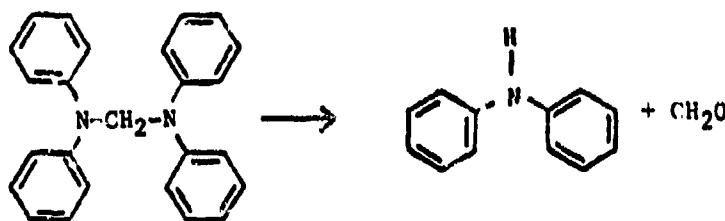
The nitration of diphenylamine in relation to its use as a propellant stabilizer has been well studied (Apatoff and Norwitz, 1973). Treatment with nitrous acid produces the nitroso, nitro- and dinitro derivatives. Prolonged treatment with the acid leads to polynitro- compounds.



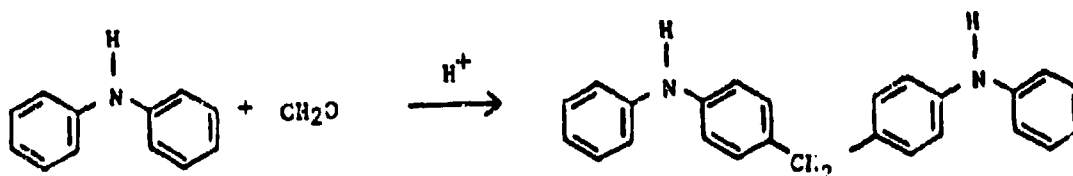
Diphenylamine reacts with formaldehyde and acetone to yield a variety of products depending upon reaction conditions (Kirk and Othmer, 1964b). Refluxing of equimolar amounts of diphenylamine and formaldehyde in benzene yields tetraphenylmethylenediamine.



Addition of dilute acids reverses the reaction.

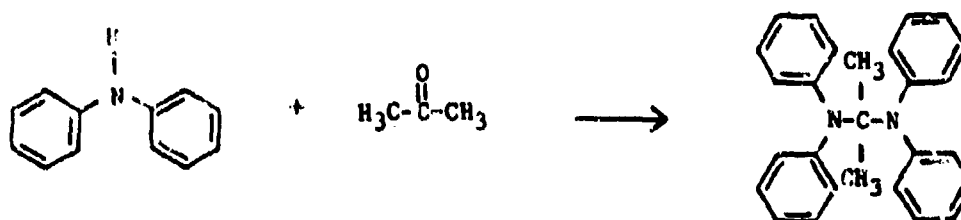


If excess diphenylamine is reacted with formaldehyde in the presence of catalytic amounts of acid, p,p'-dianilinodiphenylmethane is formed.



Prolonged heating results in polymeric resins being formed.

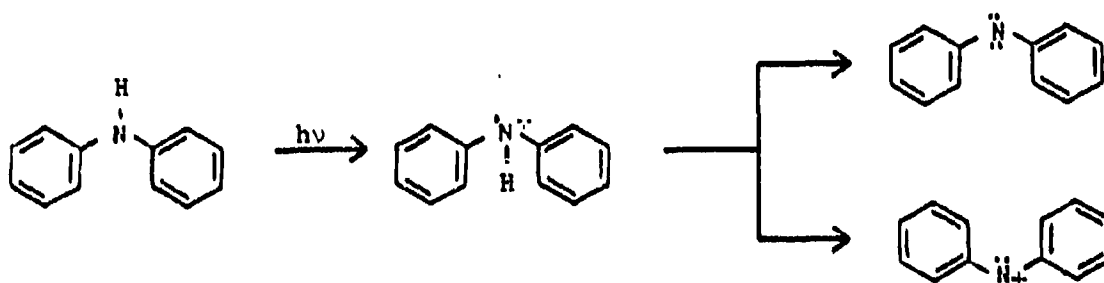
Acetone will react with excess diphenylamine in the presence of an acid catalyst to yield tetraphenyl 2,2'-diaminopropane.



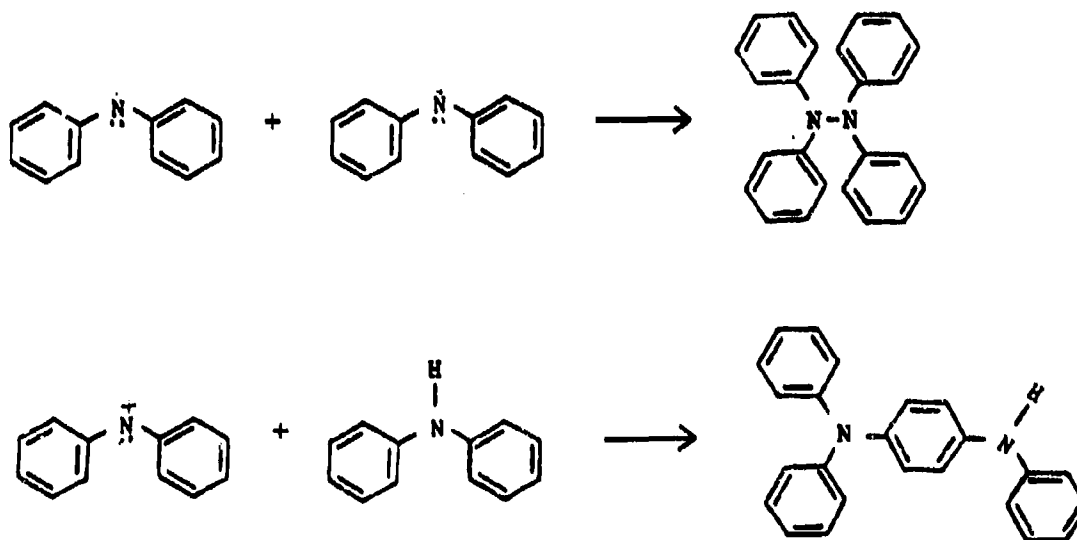
If the ketone is in excess, viscous oils containing diarylamines are formed.

## 2. Environmental Reactions

The photolysis of diphenylamine in an ether/isopentane/alcohol solution at low temperature has been investigated. Initial illumination at 250 to 300 nm results in loss of an electron. Either a proton or a hydrogen radical is lost upon continued illumination (Lewis and Lipkin, 1942).



Possible reactions between these various photolytic products include radical coupling and electrophilic substitution.



## 3. Sampling and Analysis

Most analytical techniques for diphenylamine have been developed for its determination in propellants. These techniques were recently reviewed by Apatciff and Norwitz (1973). Techniques include colorimetric determination following oxidation with nitric acid, dichromate, or ferric ion; volumetric bromination; polarographic determination; qualitative IR spectroscopy; UV spectroscopy ( $\lambda_{\text{max}} = 285 \text{ nm}$ ); thin layer chromatography; and gas chromatography (GC). GC has been used for simultaneous analysis of a number of propellant



components including diphenylamine (Sopranetti and Reich, 1972; Kelso, 1974). Diphenylamine can be determined in the presence of 2-nitrodiphenylamine, ethyl centralite, triacetin, phthalate esters, and dinitrotolulene.

Dantzman (1976) reported a spectrophotometric method for determination of diphenylamine in Ext. D&C Yellow No. 1. He was able to reliably determine diphenylamine in concentrations down to 0.02%.

#### D. Uses in Army Munitions

##### 1. Purposes

Diphenylamine is used as a stabilizer in the following propellant formulations:

	<u>% diphenylamine in formulation</u>
- CBI Powder	1.5±0.2
- IMR 1050	0.5 to 1.25
- M-1	1.0±0.2, -0.1
- M-6	1.0±0.2, -0.1
- M-10	1.0±0.3
- M6 + 2	1.0±0.2, -0.1

These formulations are single base propellants produced by the solvent process. Diphenylamine is used at all facilities which produce propellants including Badger AAP, Sunflower AAP, Radford AAP and Indiana AAP.

Diphenylamine stabilizes the propellant by reacting with NO and NO<sub>2</sub> which are formed by thermal degradation of nitrate esters. Without a stabilizer, NO and NO<sub>2</sub> will react with moisture to form nitrous and nitric acids which promote further degradation. The presence of NO<sub>2</sub> itself may cause an autocatalytic effect which also promotes degradation (Richardson, 1975). The presence of ~1% of diphenylamine in the formulation will stabilize a propellant for several years.

##### 2. Quantities Used

###### a. Historical Use

Diphenylamine is used exclusively to produce single base propellants. The predominant use is for the M-1 formulation, which accounted for 89% of the diphenylamine used at Radford AAP during 1968-1977. The average annual amount of diphenylamine purchased by Radford AAP during this period was 621,900 lb/year. The specific quantities of diphenylamine purchased by Radford AAP during the period 1968-1977 are shown below (Watts, 1978):

<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
1,229,230	930,100	772,600	348,800	346,350	767,600	839,900	337,350	94,000	133,200

b. Current Use

During 1977 Radford AAP utilized diphenylamine at an average rate of 10,000 lb/month. Based upon December 1977 production of M-1 and M-10 propellants, about 8500 lb of diphenylamine were used, or about 85% of the average rate.

c. Use at Full Mobilization

Current production of propellants which specify diphenylamine in the formulation is about 8-10% of capacity. At full mobilization, approximately 107,000 lb of diphenylamine would be used each month.

3. Documented or Speculated Occurrences in Air or Water

Diphenylamine concentrations have been measured in the effluent from the "water-dry" processing step (Glennon, 1977). The indicated loss in this step was estimated at 30-60 lb/month. This amount is not representative of total losses, however. Several other process water effluents exist which may contain diphenylamine. In addition, losses may occur in the preparation operations in which diphenylamine is weighed out and prepared for process use.

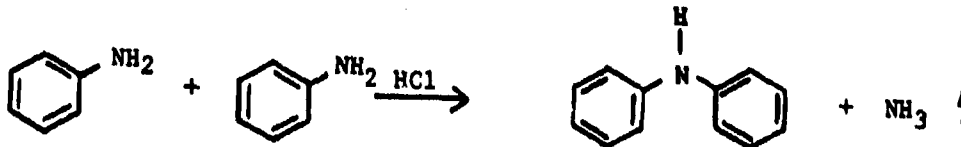
Total diphenylamine losses from both preparation and processing sources are estimated at about 300 to 500 lb/month. At full mobilization, this loss would increase to 3200 to 5300 lb/month. This represents 3-5% of the amount used, and is considered to be a typical loss level (Dickinson, 1978).

Diphenylamine is sparingly soluble in water. Since much of the material lost is collected on filters in solid form, some of the diphenylamine lost is recovered and disposed of by burning. It is estimated that about 1/3 to 1/2 of the diphenylamine lost ultimately reaches the New River as a solute in effluent streams.

E. Uses in the Civilian Community

1. Production Methodology

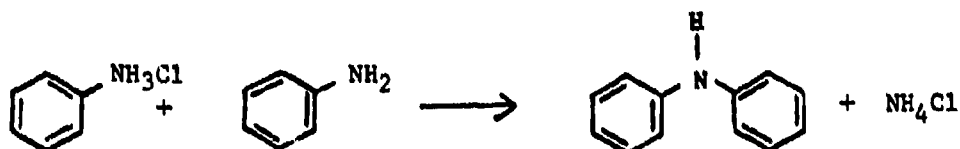
Diphenylamine is formed on an industrial scale by the self condensation of aniline in the presence of strong acids.



The reaction is conducted in an acid resistant reflux apparatus at temperatures around 300°C and high pressure. Aniline combines with the acid to form aniline hydrochloride.



The aniline hydrochloride combines with a second molecule of aniline to form diphenylamine and ammonium hydrochloride.



In the presence of excess aniline, ammonium hydrochloride decomposes to ammonia and hydrochloric acid, regenerating the catalyst. The ammonia is removed at the top of the column. The crude product is washed with aqueous sodium carbonate to remove any traces of acid and then vacuum distilled. The yield approaches 80% (Kirk and Othmer, 1964d).

## 2. Manufacturers, Production and Capacity

There are two manufacturers of diphenylamine in the U.S. American Cyanamid manufactures this chemical in Bound Brook, N.J. and Rubicon Chemicals has a plant in Geismar, La. Plant capacities are unavailable. In 1977, American Cyanamid increased their capacity by 50%. Rubicon has scheduled expansion to be completed late this year which will increase their capacity by 26 million pounds per year (S.R.I., 1977). Historical production figures are listed below in Table III-2 (U.S. Tariff Commission).

Table III-2. U.S. Production of Diphenylamine\*.

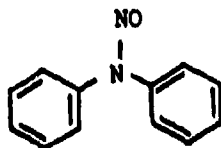
<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>
32.2	34.8	29.4	30.6	33.8	34.7	39.9

\* in million pounds

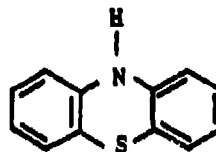
## 3. Usages

Diphenylamine is used in the dye industry as an intermediate for a variety of dyes including Metanil Yellow, Aniline Yellow, Curcumine, Alkali Green, and Pyrogene Indigo (Kirk and Othmer, 1964a).

It is also used as an antioxidant for rubber, as a colorimetric indicator in analyses, and as a chemical intermediate to N-nitrosodiphenylamine and phenothiazine.



N-nitrosodiphenylamine



Phenothiazine

#### 4. Future Trends

The diphenylamine market is stable with growth expected to parallel the rubber and dye industries.

#### 5. Documented or Speculated Occurrences in the Environment

Diphenylamine has not been reported as an environmental contaminant in the civilian community. It is known to be present in Ext. D&C Yellow No. 1. It is required to be in concentrations below 0.2% (Dantzman, 1976).

#### F. Comparison of Military and Civilian Uses and Pollution

According to the latest available figures for civilian diphenylamine production, 39.9 million pounds of this amine were produced in the U.S. in 1974. Radford AAP's use of diphenylamine in 1974 was 839,900 or about 0.02% of the diphenylamine produced by the civilian manufacturers. At full mobilization, Radford AAP would use about 1,284,000 lb/year of diphenylamine. If the use rate at Badger or Sunflower and Indiana were about the same as Radford AAP, the Army would use about 5,136,000 lb/year at full mobilization. This use rate would be ~13% of the 1974 civilian production of diphenylamine.

#### G. Toxicological and Environmental Hazards

##### 1. Mammalian Toxicology

Diphenylamine is moderately toxic to mammals. Lande *et al.* (1934) administered oral doses of 0.5-2.0 g/kg of diphenylamine to rabbits. They observed a loss of body weight and asthenia. Some deaths occurred in 15-20 days. Thomas *et al.* (1967) exposed rats to diphenylamine in their food for almost 2 years. At the end of 240 days, they observed weight differences between the control and the male rats which were fed 0.5 and 1% diphenylamine. Differences between controls and the female rats fed 0.1, 0.5 and 1% diphenylamine were also observed. Thomas's group also found a significant

difference ( $P < .05$ ) in mean number per litter between controls and the rats fed 0.5% diphenylamine in the first mating; and controls and the rats fed 0.1% diphenylamine in the second mating. Abood and Romanchek (1957) found that diphenylamine concentrations of  $10^{-4}$  M produced a 23% inhibition in rat brain mitochondria. Alexander et al. (1975) administered oral doses of diphenylamine to rats, rabbits and men. They found the major metabolites were 4-hydroxydiphenylamine and 4,4'-dihydroxydiphenylamine.

From these studies, it appears that diphenylamine is moderately toxic to mammals. Recently Safe et al. (1977) identified toxic impurities in commercial diphenylamine. Table III-3 shows the varying amounts of impurities in 6 brands of diphenylamine. One of the impurities, 4-aminobiphenyl, has been shown to be carcinogenic. Orjelick (1975) stated that diphenylamine had a strong association with bladder cancer, not on its own, but because 4-aminobiphenyl was usually present as an impurity. 4-aminobiphenyl has been shown to induce tumors in the liver and intestines of rats and cancer of the bladder in dogs (Walpole et al., 1954). Koss et al. (1969) found cancer of the bladder in workers exposed to 4-aminobiphenyl.

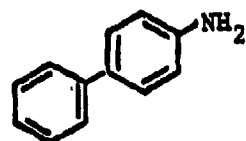
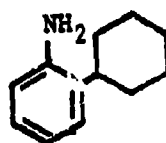
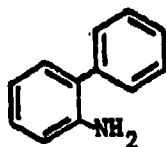
Thus, while diphenylamine itself is only moderately toxic, commercial diphenylamine can be contaminated with the carcinogen, 4-aminobiphenyl. The amount of 4-aminobiphenyl in the diphenylamine used by the Army should be determined. The previous toxicity studies on diphenylamine should be re-evaluated if a commercial grade of diphenylamine was used in the tests.

## 2. Aquatic Toxicology

Levels of diphenylamine in the aquatic environment have not been measured. The acute toxicity of diphenylamine to aquatic organisms is shown in Table III-4. Diphenylamine is most toxic to *Daphnia magna* with a 48 hour LC50 of 0.35 ppm. Hartley (1977) estimated a safe level of diphenylamine to aquatic organisms to be 12 ppb.

Radford AAP's current use of diphenylamine is about 10,000 lb/month. Under full mobilization, 107,000 lb/mo would be used. Based upon anticipated losses from preparation, and processing steps, 150-250 lb/mo diphenylamine would be released to the New River under current production rates. At full mobilization, release of 1600-2600 lb/mo of diphenylamine into the waste stream is possible. The concentrations of diphenylamine that could occur at different flow rates and mixing concentrations are shown in Table III-5. Based on Hartley's (1977) estimated safe level of 12 ppb for diphenylamine, diphenylamine can be acutely toxic to aquatic organisms near the Radford AAP discharge point. During full mobilization, a much greater area of the river could be contaminated and massive kills of aquatic organisms could occur.

Table III-3. Toxic Impurities in Commercial Diphenylamine \* (Safe et al., 1977).



<u>Commercial</u> <u>DPA</u>	<u>Band 1</u> <u>(ppm)</u>	<u>Band 2</u> <u>o-biphenyl-</u> <u>amine (ppm)</u>	<u>Band 3</u> <u>o-cyclohexyl-</u> <u>aniline (ppm)</u>	<u>Band 4</u> <u>p-biphenyl-</u> <u>amine (ppm)</u>
Brand 1	50	-	93	-
Brand 2	45	32	22	94
Brand 3	12	22	17	27
Brand 4	9	3.2	5	17
Brand 5	-	-	48	6.9
Brand 6	-	-	12	-

\* Brand 1 contains an additional impurity (i.e., Band 5) identified as p-cyclohexylaniline

Table III-4. Acute Toxicity of Diphenylamine to Aquatic Organisms.

<u>Species</u>	<u>24 Hours</u>	<u>48 Hours</u>	<u>96 Hours</u>	<u>Reference</u>
Water Flea ( <i>Daphnia magna</i> )	1.0	0.35	-	Warner et al., 1978
Fathead Minnow ( <i>Pimephales promelas</i> )	3.2	3.2	1.52	Warner et al., 1978
Bluegill ( <i>Lepomis macrochirus</i> )	-	-	1.10	Hartley, 1977
Ostracod ( <i>Cylocypris</i> sp.)	-	2.53	-	Hartley, 1977

Table III-5. Levels of Diphenylamine (ppm) in the New River at Full Mobilization.

<u>Degree of Mixing</u>	<u>Low Flow (336 mgd)</u>	<u>Average Flow (2500 mgd)</u>
1%	3.1	0.4
10%	0.31	0.04
100%	0.03	0.004

Due to its insolubility, diphenylamine would eventually accumulate in the sediment. Its persistence in the sediment could increase diphenylamine's toxicity to aquatic organisms. The availability of diphenylamine to aquatic organisms and possible biomagnification through the aquatic food levels are unknown. In the presence of nitrate and a high pH, N-nitrosodiphenylamine and tetra-nitrodiphenylamine can be formed. 2:1 diphenylamine and formaldehyde complexing can also occur.

### 3. Toxicity to Microorganisms and Plants

The toxicity of M-1 propellant dust to aquatic ecosystems has been investigated by Hartley (1977). In algae studies with *Microcystis aeruginosa*, culture death was found after a seven day exposure to 5 mg/l of diphenylamine.

Studies with sewage treatment microorganisms showed no adverse effects on the sewage treatment organisms after exposure to 111.3 mg/l of M-1 propellant. The degree of biodegradation of the M-1 propellant by these organisms is not known (Hartley, 1977).

### 4. Environmental Fate

Experimental evidence indicates that diphenylamine may be microbiologically transformed into carcinogenic compounds. Hawksworth and Hill (1971) reported that 27 of 37 strains of coli and a proportion of strains of other faecal aerobes and anaerobes were able to produce nitrosamines from nitrate and diphenylamine at a pH above 6.5. These nitrosamines can be further degraded. However, their effect on the environment is not resolved.

### 5. Availability of Literature for Phase II

Sufficient literature sources on the toxicology and environmental fate of diphenylamine were identified during the preliminary study to indicate the availability of sufficient information for Phase II.

## H. Regulations and Standards

### 1. Air and Water Regulations

The EPA has issued effluent limitations guidelines for discharges from the manufacture of diphenylamine (Federal Register, 1976). These effluent guidelines are listed in Table III-6. Diphenylamine is listed in EPA's Toxic Control Act Candidate List of Chemical Substances (1977). However, there are no immediate plans for any EPA sponsored work on this chemical.

### 2. Human Exposure Standards

A TLV of 10 mg/m<sup>3</sup> for diphenylamine has been suggested by the American Conference of Governmental Industrial Hygienists (1977). This compound is not listed on NCI suspected carcinogenic list (NIOSH, 1975).



Table III-6. Effluent Guidelines for the Manufacture of Diphenylamine  
(Federal Register, 1976).

<u>Effluent Characteristic</u>	<u>Effluent Limitations</u>	
	Maximum for Any 1 Day	Average of Daily Values for 30 Consecutive Days Shall Not Exceed:
	1b/1000 lb of Product	
BOD 5	0.041	0.021
TSS	0.062	0.033
pH	Within the range 6.0 to 9.0	

#### I. Conclusions and Recommendations

The goal of this preliminary problem definition study was to determine the Army's responsibility for conducting future research on diphenylamine. From the data presented in this report, the following conclusions have been drawn

1. Diphenylamine is not a military unique chemical; it is widely used throughout the dye and rubber industries.
2. Reliable figures on the pollution resulting from the civilian and military use of this chemical are not available. However it is estimated that ~ 5% of this pollution results from Army propellant production.
3. Diphenylamine itself is only moderately toxic to mammals, however, significant quantities of the carcinogenic, 4-aminobiphenyl, have been found to be present as impurities in the commercial product.
4. Further mammalian toxicological studies on diphenylamine should be conducted by the civilian community.
5. Diphenylamine is highly toxic to aquatic organisms. Radford AAP operations could lead to significant effects on the aquatic system from this compound.
6. Further evaluation of the discharges and aquatic ecosystems stress from military operations using diphenylamine is warranted.

The following recommendations are made based on the results of this preliminary problem definition study.

- In order to protect workers exposed to diphenylamine, the Army should investigate the amount of 4-aminobiphenyl in its purchased diphenylamine.

- Further mammalian toxicological studies on diphenylamine are mainly a civilian problem.

- The levels of discharges of diphenylamine from Radford and Indiana AAP require further quantitation. A planned effluent analysis program should be undertaken to obtain this information.

- Further evaluation of the environmental toxicity and fate of this compound should be undertaken. The initial step in this study should be a Phase II literature evaluation of the environmental problems and fate associated with diphenylamine.

- Additional experimental studies to define the environmental fate of diphenylamine and the ability of planned treatment processes to remove this compound from Radford AAP's wastes may be necessary depending on the outcome of the literature evaluation.

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PRELIMINARY PROBLEM DEFINITION STUDY OF  
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VOLUME II PROPELLANT RELATED CHEMICALS

DIETHYLENEGLYCOL DINITRATE

FINAL REPORT

J. F. Kitchens  
W. E. Harward III  
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R. S. Valentine

April 1978

Supported by:

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Fort Detrick, Frederick, Maryland 21701

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## SUMMARY

Diethyleneglycol dinitrate is used exclusively as a high energy plasticizer for propellants. Current U. S. production capacity is 25,000 lb/year. The only Army use of this chemical in the past several years has been three 55 gallon drums. This material was produced and used at Radford AAP for formulation of M-37 propellants.

No specific mammalian or aquatic toxicity data on diethyleneglycol dinitrate was obtained. By extrapolation of available data on other organic nitrates, this compound should be moderately toxic to both mammals and aquatic organisms. In the aquatic environment, it probably accumulates in the sediment and is slowly degraded either by acidic conditions or microorganisms.

It is recommended that this compound not be evaluated in Phase II. If future plans call for large production of M-37, then a detailed evaluation of the toxicological and environmental hazards of diethyleneglycol dinitrate by the Army would be warranted.

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## FOREWORD

This report details the results of a preliminary problem definition study on diethyleneglycol dinitrate. The purpose of this study was to determine the Army's responsibility for conducting further research on diethyleneglycol dinitrate in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on diethyleneglycol dinitrate, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Diethyleneglycol dinitrate was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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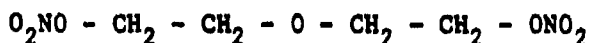
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#### IV. DIETHYLENEGLYCOL DINITRATE

##### A. Alternate Names

Diethyleneglycol dinitrate is an explosive possessing the following chemical structure:



It has a molecular formula of  $\text{C}_4\text{H}_8\text{N}_2\text{O}_7$  corresponding to a molecular weight of 196.1g/mole. Pertinent alternate names for diethyleneglycol dinitrate are listed below:

CAS Registry No.:	693-21-0
CA Name (9 CI):	Ethanol, 2,2'-oxybis-dinitrate
CA Name (8 CI):	Diethyleneglycol, dinitrate
Wiswesser Line Notation:	
Synonyms:	DEGN, Diglycol dinitrate; Dinitrodiglycol; Dinitroglycol; Oxydiethylene nitrate

##### B. Physical Properties

The physical properties of diethyleneglycol dinitrate are presented in Table IV-1.

Table IV-1. Physical Properties of Diethyleneglycol dinitrate.\*

Physical Form @ 20°C:	liquid
Color:	yellow
M.P.:	-11.3°C
B.P.:	161°C
Liquid Density, $d_4^{25}$ :	1.377 g/ml
Vapor Density, (air=1):	6.7 g/ml
Vapor Pressure:	0.0036 mm Hg @ 20°C
Viscosity @ 20°C:	8.1 cP
Heat of Combustion:	2792 cal/gm
Refractive Index, $n_D^{25}$ :	1.4498
Solubility:	water - 0.40 g/100g @ 20°C 0.60 g/100g @ 60°C slightly soluble in alcohol soluble in ether

\*References: Sax, 1976; Hawley, 1977; Army Materiel Command, 1971.

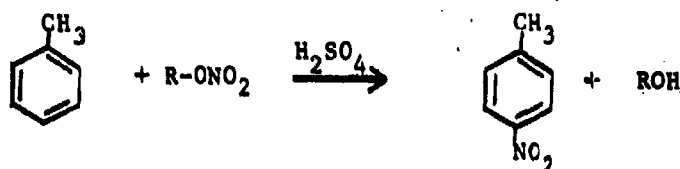
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### C. Chemical Properties

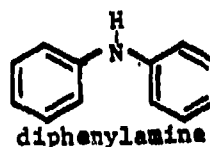
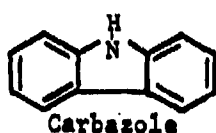
#### 1. General Reactions

Although the chemistry of certain alkyl nitrates (methyl, ethyl, tert-butyl) has been investigated, the chemistry of diethyleneglycol dinitrate has not been widely reported. Much of this chemistry must be inferred from the behavior of the simpler nitrate esters.

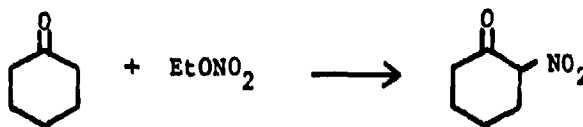
Nitrate esters are capable of transferring the  $\text{NO}_2$  function to other systems (Boschan *et al.*, 1955). Toluene is easily nitrated in 98%  $\text{H}_2\text{SO}_4$  with ethyl, n-butyl, and  $\beta$ -chloroethyl nitrate.



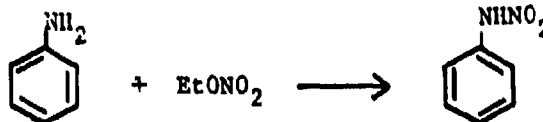
Lewis acids such as  $\text{AlCl}_3$  can catalyze this reaction. Ethyl nitrate has been used in the nitration of other aromatic systems including carbazole, a compound resembling diphenylamine.



Nitrate esters can also be used for nitration of certain active methylene groups.

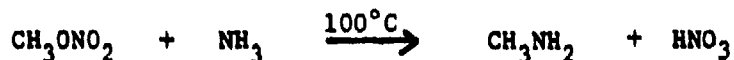


N-nitration also is observed. The reaction of ethyl nitrate and aniline in the presence of either sodium in ether or ethoxide anion yields phenylnitramine.



N-nitrosation may occur. The reaction between diphenylamine and ethylnitrate yields N-nitrosodiphenylamine along with other products.

Nitrate esters are known to act as alkylating agents in their reaction with certain nucleophiles. Heating nitrate esters with ammonia, or primary or secondary amines results in N-alkylation.



Alcoholysis, the reaction of nitrate esters with alcohols, involves O-alkylation to form mixed ethers.



Nitrate esters can be reduced to the corresponding alcohol by any number of standard techniques including electrolysis, hydrogenolysis, or treatment with metal hydrides or metals in acid (Boschan *et al.*, 1955).

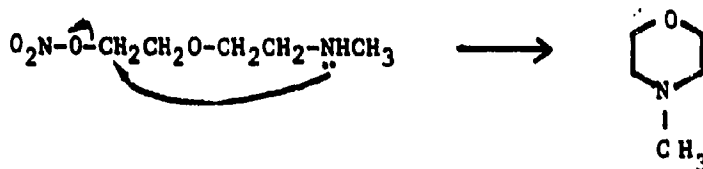
Diethyleneglycol dinitrate can be expected to undergo these typical reactions of nitrate esters. The presence of the second ester function in the molecule makes certain further reactions possible.

During hydrolysis (to be discussed in the following section) or its action as a nitrating agent, diethyleneglycol dinitrate is transformed to diethyleneglycol mononitrate. The monoester is capable of cyclization.



Dioxane can be expected to form due to the combined effects of the proximity of the nucleophilic alcohol function and the generation of a thermodynamically favorable ring.

In the reaction of diethyleneglycol dinitrate with ammonia or primary amines, another cyclization is possible. The amino function of the first formed product may behave as an intra-molecular nucleophile yielding N-substituted morpholines.



## 2. Environmental Reactions

Diethyleneglycol dinitrate is fairly stable to hydrolysis. Heating at 60°C for 5 days resulted in only 0.003% decomposition. Hydrolysis in the

presence of mixed acids resulted in approximately 1% cleavage to the monoester after 6 hours (Urbanski, 1965).

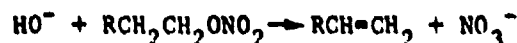
It has long been known that hydrolysis of nitrate esters yields more than the simple alcohol and nitrate anion. The three separate processes which complete in nitrate ester cleavage are represented in Figure IV-1.

Figure IV-1. Nitrate Ester Hydrolysis.

a)  $SN_1$  or  $SN_2$



b)  $E_2$

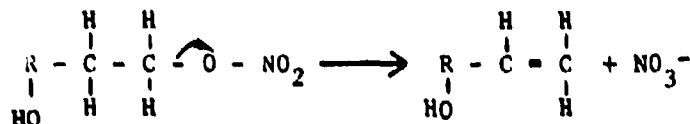


c) Elimination of an  $\alpha$  proton



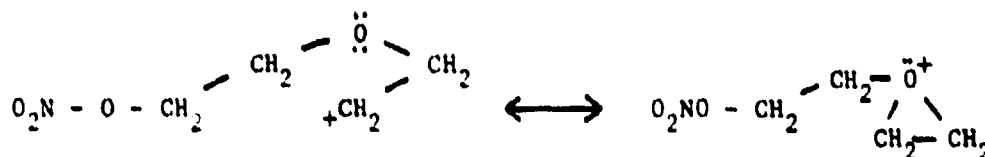
Reaction a) involves displacement of the nitrate group by nucleophilic hydroxide anion. In near neutral solutions water molecules may act as nucleophiles. Most esters undergo bimolecular substitution ( $SN_2$ ) with nucleophilic addition and elimination of nitrate occurring simultaneously. Sterically hindered nitrate esters generally are hydrolyzed via  $SN_1$  processes involving initial loss of nitrate to form a carbonium ion followed by rapid addition of a water molecule.

Reaction b) involves simultaneous elimination of a  $\beta$  proton and the  $NO_3^-$  moiety.



Reaction c) proceeds with abstraction of an  $\alpha$  proton with simultaneous cleavage of the O-N bond rather than the C-O bond (Boschan et al., 1955).

Hydrolysis of diethyleneglycol dinitrate will give mostly nitrate ion and diethyleneglycol mononitrate. The reaction may proceed via an  $SN_1$  mechanism, an  $SN_2$  mechanism, or both processes may compete. Generally primary nitrate esters will not undergo  $SN_1$  type reactions due to the low stability of primary carbonium ions. Diethyleneglycol dinitrate is an exception due to resonance stabilization of the carbonium ion by the ether oxygen.



In neutral solutions where the strong  $\text{OH}^-$  nucleophile is not present, the importance of the  $\text{SN}_2$  mechanism will increase.

Hydrolysis of diethyleneglycoldinitrate via reactions b) and c) will be of roughly equal, though extremely minor, importance. The presence of bases in the water will magnify their importance.

### 3. Sampling and Analysis

Several methods have been developed to determine the alkylpolynitrates in air and water samples. Quantitative separation and analysis of alkylpolynitrates by gas chromatography with a hot wire detector was reported by Camera and Pravisani (1964). They used short columns and low temperatures to prevent decomposition reactions. The method gave good separations and high precision. However, no lower detection was given.

Detection of nitrate esters in water to the 20 ppb level is possible using a single-sweep polarographic method (Whitnack and Beckett, 1976). This system was developed for the Navy to monitor 1,2-propyleneglycol dinitrate in their effluent. The method can be used as a continuous monitor in a range of 0.10 to 1000 ppm 1,2-propyleneglycol dinitrate in water.

Two methods of analysis of low concentrations of nitrate esters in air are reported in the literature. One method is based upon nitration of m-xylene in a sulfuric acid collection solution. The nitroxylene is determined colorimetrically after isolation by steam distillation (Yagoda and Golderson, 1943). In a gas chromatographic method, Camera and Pravisani (1967) collected air samples by bubbling through ethanol. The ethanol solutions were injected directly into a gas chromatograph equipped with an electron capture detector. With a 10 l air sample volume, the sensitivities for various nitrate esters were

- ethyleneglycol dinitrate 0.08  $\text{mg/m}^3$
- 1,2-propyleneglycol dinitrate 0.02  $\text{mg/m}^3$

### D. Uses in Army Munitions

#### 1. Purposes

Diethyleneglycol dinitrate is used to produce the M-37 propellant formulation. M-37 is manufactured by the solventless process. The formulation is produced infrequently. At Radford AAP it has only been produced one time in the plant's history, and that was in 1977. It has not been made in

the other propellant manufacturing AAP's in recent years. Diethyleneglycol-dinitrate is produced on site at Radford AAP when needed by nitration of diethyleneglycol.

## 2. Quantities Used

### a. Historical Use

A total of three 55 gallon drums (~1500 lb) of diethylene-glycol dinitrate were produced and used at Radford AAP in 1977.

### b. Current Use

Diethyleneglycol dinitrate is not currently used at Radford AAP, and no future use is contemplated.

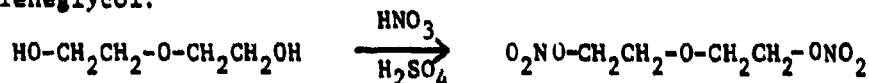
## 3. Documented or Speculated Occurrences in Air or Water

The one-time use of diethyleneglycol dinitrate at Radford AAP probably resulted in no more than 15-30 lb of the material entering the environment. The point of entry was the waste effluent from the rolled powder area.

## E. Uses in the Civilian Community

### 1. Production Methodology

Diethyleneglycol dinitrate is produced by the mixed acid nitration of diethyleneglycol.



The reaction temperature must be kept low to prevent hydrolysis and oxidation. Industrial scale yields are maximized at temperatures between 10 and 15°C with a 50:45:5 mixture of HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub>: water. The weight ratio of acid mixture to diol is 3.67 to 1. The industrial yield is reported at 85% (Urbanaki, 1965).

### 2. Manufacturers, Production and Capacity

Diethyleneglycol dinitrate is manufactured by the Trojan U.S. Powder Division of the IMC Chemical Group, Inc. The plant site is 55 miles south of Salt Lake City near Spanish Fork, Utah. They produce diethyleneglycol dinitrate on order. Their current facilities have a capacity of twenty-five thousand pounds per year which could be tripled with minor modifications (Trojan, 1977).

### 3. Usages

Diethyleneglycol dinitrate has no applications other than a high energy plasticizer for propellants.



#### 4. Future Trends

No new civilian uses for diethyleneglycol dinitrate are anticipated.

#### 5. Documented or Speculated Occurrences in the Environment.

There are no reported occurrences of diethyleneglycol dinitrate in the environment from civilian manufacture.

#### F. Comparison of Military and Civilian Usages and Pollution

Diethyleneglycol dinitrate is produced in both the military and civilian sectors on demand. It is not a high quantity item or a high quantity polluter in either sector. Therefore, it does not represent a continuous threat to the environment. With proper handling, it should not escape into the environment in any significant quantities on those occasions when it is manufactured.

#### G. Toxicological and Environmental Hazards

##### 1. Mammalian Toxicity

The toxicity of diethyleneglycol dinitrate has not been studied in detail. However, all the nitrate esters are toxic to varying degrees. Their toxicity is due to their ability to oxidize hemoglobin to methemoglobin. They also depress vascular wall muscles causing peripheral vasodilation. This vasodilator action results in a decrease in systolic blood pressure and an increase in pulse and respiratory rates. The main symptom of nitrate ester poisoning is a severe pressure headache. Vertigo or fainting may also result (American Conference of Governmental Industrial Hygienists, 1971).

##### 2. Aquatic Toxicity

Little, if any, research has been conducted on the distribution of diethyleneglycol dinitrate in the aquatic environment. In its one time use at Radford AAP, 165 gallons of diethyleneglycol were nitrated. Probably no more than 15 to 30 lb, if this much, were lost to the New River. Since diethyleneglycol dinitrate is heavier than and insoluble in water, it will be found in the sediment. Hydrolysis should occur only very slowly in the River. If this degradation occurs, microorganisms in the sediment could then further degrade the diethyleneglycol.

##### 3. Toxicity to Invertebrates, Microorganisms and Plants

No information was retrieved on the toxic effects of diethyleneglycol dinitrate on microorganisms, invertebrates or plants.

#### 4. Availability of Literature for Phase II

No toxicological or environmental literature specific to diethyleneglycol dinitrate was found in this preliminary study. Toxicological data may be found in the older and foreign literature.

#### H. Regulations and Standards

There are no specific standards for diethyleneglycol dinitrate. However, a TLV of 0.20 ppm (1.5 mg/m<sup>3</sup>) for skin exposure is recommended for 1,2-propyleneglycol dinitrate (American Conference of Governmental Industrial Hygienists, 1971). This value is also the maximum acceptable dose. A similar TLV for diethyleneglycol dinitrate would be expected.

Diethyleneglycol dinitrate is not listed in EPA Toxic Substances Control Act List of Candidate Chemicals (1977). DOT forbids shipment of diethyleneglycol dinitrate (Federal Register, 1976).

#### I. Conclusions and Recommendations

Diethyleneglycol dinitrate is not used to any extent by either the military or civilian sectors. The largest use of this chemical appears to be in civilian propellant production. Diethyleneglycol dinitrate was used once at Radford AAP in M-37 propellant. Thus, this compound does not present a military use or pollution problem unless the production of large quantities of M-37 propellant are anticipated in the future. Therefore, it is recommended that diethyleneglycol dinitrate only be evaluated in Phase II if production of large quantities of M-37 is anticipated in the future.

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PRELIMINARY PROBLEM DEFINITION STUDY OF  
48 MUNITIONS-RELATED CHEMICALS

VOLUME II PROPELLANT RELATED CHEMICALS

2-NITRODIPHENYLAMINE

FINAL REPORT

J. F. Kitchens  
W. E. Harvard III  
D. M. Lauter  
R. S. Wentzel  
K. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND  
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION  
Alexandria, Virginia 22314

Approved for Public Release  
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

AD

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## SUMMARY

2-Nitrodiphenylamine is widely used as a stabilizer in double-base solid propellant formulations. It is found in the formulations in concentrations of 0.9 to 3.0%. Radford is the only operational Army Ammunition Plant which is using 2-nitrodiphenylamine. Badger and Sunflower also use this compound when they are operational.

Current use rate of 2-nitrodiphenylamine at Radford AAP is ~6000 lb/month. At full mobilization the Radford AAP use rate for this compound is 6000 - 7000 lb/month. It is expected that at full mobilization the usage of 2-nitrodiphenylamine at the Badger and Sunflower AAPs would be approximately the same as at Radford AAP. Thus a total of 252,000 lb/year of 2-nitrodiphenylamine could be used by the Army.

There is only one civilian producer of 2-nitrodiphenylamine. The civilian capacity is estimated at >250,000 lb/year. The only civilian use of 2-nitrodiphenylamine is as a chemical intermediate in the dye industry. However, civilian companies that make solid rockets could purchase some of this compound. The extent of these purchases is unknown.

At current production levels, Radford utilizes ~40% of the estimated civilian production capacity of 2-nitrodiphenylamine. With three plants at full mobilization, the Army would purchase ~100% of the estimated civilian production capacity of this chemical. Under current operational conditions, the Army is also one of the main polluters of 2-nitrodiphenylamine. The percentage of the total 2-nitrodiphenylamine pollution emanating from Army propellant manufacturing is impossible to determine, due to the unavailability of civilian production statistics.

Limited mammalian toxicology studies indicate 2-nitrodiphenylamine is not very toxic in acute doses (LD50 for rats = 6.15 g/kg). Limited studies concerning the toxicity of 2-nitrodiphenylamine to fish and invertebrates show that this compound is highly toxic to aquatic organisms with LC50's ranging from 1.8 to 5.6 ppm. Reaction of 2-nitrodiphenylamine in the environment could lead to more toxic compounds.

Although 2-nitrodiphenylamine is not a military unique compound the military is one of the major users and polluters of this chemical. Preliminary evidence indicates a high potential environmental danger from 2-nitrodiphenylamine. It is therefore recommended that 2-nitrodiphenylamine be included in the Phase II detailed toxicological and environmental studies.

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## FOREWORD

This report details the results of a preliminary problem definition study on 2-nitrodiphenylamine. The purpose of this study was to determine the Army's responsibility for conducting further research on 2-nitrodiphenylamine in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on 2-nitrodiphenylamine, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

2-nitrodiphenylamine was only one of the 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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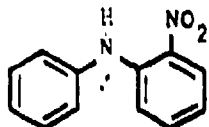
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## V. 2-NITRODIPHENYLAMINE

### A. Alternate Names

2-nitrodiphenylamine has the following structure:



and a corresponding molecular formula of  $C_{12}H_{10}N_2O_2$ . It has a molecular weight of 214.23g/mole. Pertinent alternate names for 2-nitrodiphenylamine are listed below:

CAS Registry No.:	119-75-5
CA Name (9CI):	Benzenamine, 2-nitro-N-phenyl-
CA Name (8CI):	Diphenylamine, 2-nitro-
Wiswesser Line Notation:	WNR BMR
Synonyms:	C.I. 10335; 2-nitrodiphenylamine; o-nitro-N-phenylaniline; o-nitro- diphenylamine; Sudan Yellow 1339

### B. Physical Properties

The physical properties of 2-nitrodiphenylamine are presented in Table V-1.

---

Table V-1. Physical Properties of 2-nitrodiphenylamine\*.

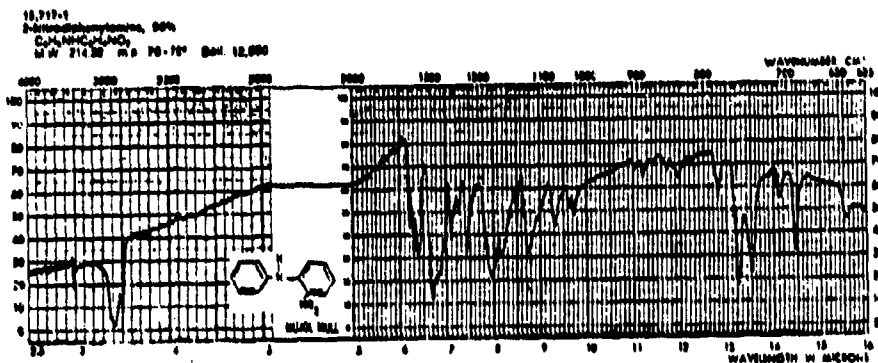
Physical Form @ 20°C:	orthorhombic crystals
Color:	red-brown
M.P.:	75-76°C
B.P.:	223 @ 20 mmHg
Specific Gravity:	1.366

\* References: Prasad and Shanker, 1936; Hawley, 1977; Lange, 1946

---

The infrared spectrum of this compound is shown in Figure V-1.

Figure V-1. Infrared Spectrum of 2-nitrodiphenylamine  
(Pouchert, 1975).



The ultraviolet spectrum of 2-nitrodiphenylamine in methanol shows three absorption maximum (CRC, 1974):

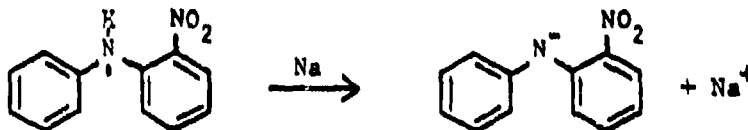
$\lambda_{\text{max}}$ = 424 nm	$\epsilon$ = 6,770
258 nm	14,400
218 nm	13,700

### C. Chemical Properties

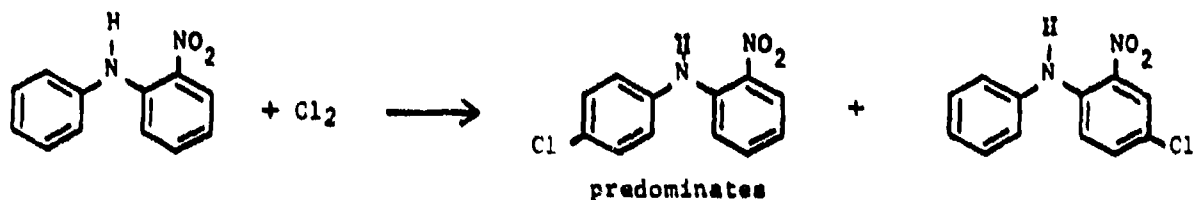
#### 1. General Reactions

The chemistry of 2-nitrodiphenylamine has not been widely reported in the literature. Its chemical behavior can be expected to parallel structurally similar compounds. Much of the chemistry of diphenylamine should be applicable to the 2-nitro derivative.

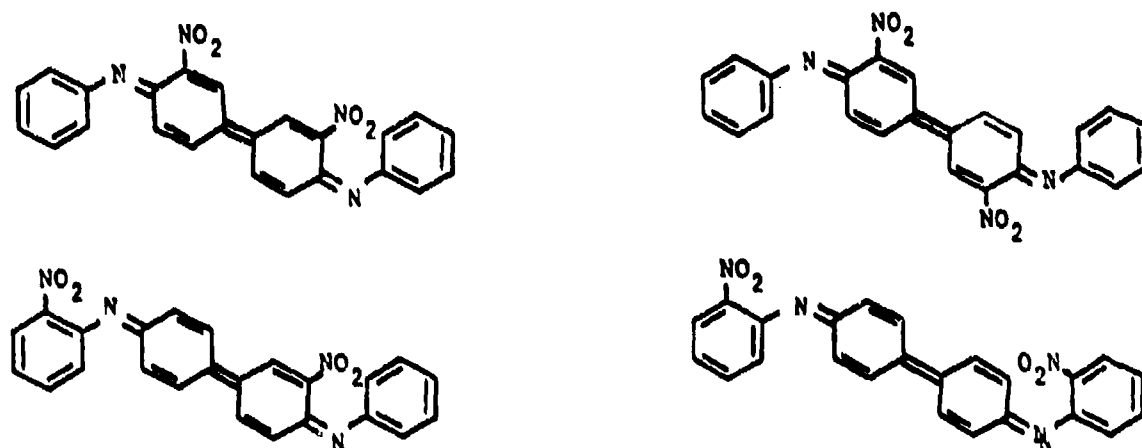
The amine proton should be labile. Treatment with sodium metal will form the anion (Kirk and Othmer, 1964).



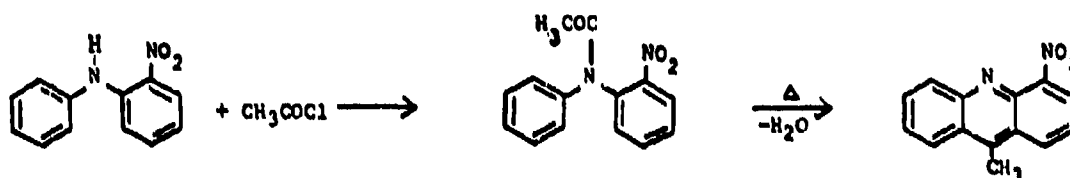
2-nitrodiphenylamine will easily undergo electrophilic aromatic substitution. Substitution will occur primarily on the un-nitrated ring.



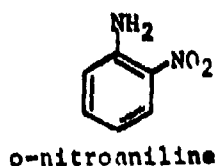
Oxidative coupling of two molecules is possible. Nitrogen-nitrogen coupling will be more difficult due to increased steric hindrance. Coupling through the aromatic rings could lead to a mixture of four products (Kirk and Othmer, 1964).



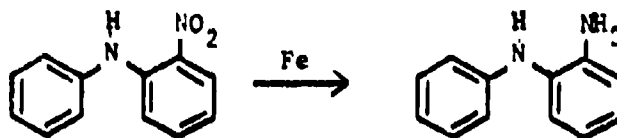
Treatment with an organic acid chloride followed by heating may form nitro-acridines (Kirk and Othmer, 1964).



2-nitrodiphenylamine is also structurally similar to o-nitroaniline.

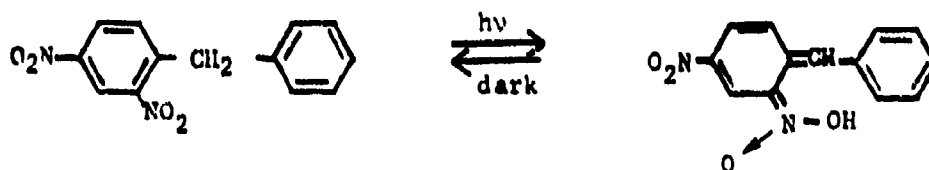


o-nitroaniline is reduced to phenylenediamine by iron (Schenk, 1960). An analogous reduction of 2-nitrodiphenylamine would be expected to yield 2-aminodiphenylamine.

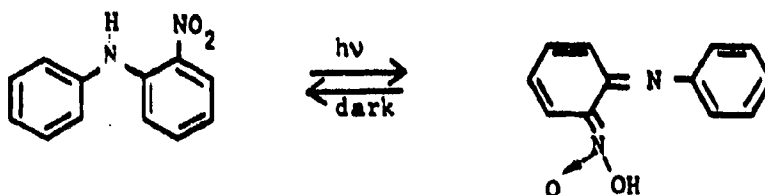


## 2. Environmental Reactions

The photochemistry of 2-nitrodiphenylamine has not been reported in the literature. It might be expected to parallel the photolyses of either diphenylamine or nitrobenzene. More likely, 2-nitrodiphenylamine will exhibit photochromism, a photoinduced isomerization, analogous to 2,4-dinitrodiphenylmethane (Dessauer and Paris, 1963).



Upon irradiation, 2-nitrodiphenylamine would isomerize to its photochrome. The reaction would reverse itself thermally.



## 3. Sampling and Analysis

Analytical techniques for 2-nitrodiphenylamine have been developed primarily for its determination in propellant compositions. Gas chromatography allows determination of 2-nitrodiphenylamine in single and double base propellant extracts. Low injection port temperatures must be used to avoid decomposition of nitroglycerin resulting in nitrations. Analyses of triacetin, phthalate esters, resorcinol, and dimethyl sebacate are carried out simultaneously (Trowell and Philpot, 1969; Trowell, 1970).

2-nitrodiphenylamine can be determined spectrophotometrically by UV absorbance at 420 nm. Dry column chromatography has been reported as a

successful extractive technique (Landram *et al.*, 1970).

Liquid chromatography has been recently developed for the analysis of 2-nitrodiphenylamine. UV absorbance at 254 mμ allows quantitative determination. This technique has been shown to allow reliable analysis of 2-nitrodiphenylamine in the presence of dinitrodiphenylamine derivatives (Doali and Juhasz, 1975).

D. Uses in Army Munitions

1. Purposes

2-nitrodiphenylamine is widely used as a stabilizer in propellant formulations, although generally in small quantities. Formulations which specify 2-nitrodiphenylamine are listed in Table V-2. These propellants

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Table V-2. Use of 2-nitrodiphenylamine in Propellants  
(Hercules Inc., 1977).

<u>Formulation</u>	<u>% 2-nitrodiphenylamine in formulation</u>
AAH Casting Powder	1.0±0.15
ARP Casting Powder	2.0±0.15
PNJ Casting Powder	1.95
N-5	2.0
N-14	2.0±0.5
NOSIH-AA-2	2.0±0.5
NOSIH-AA-6	2.0
M-36	1.5±2.5
NOSIH-AM-2	2.0±0.5
N-12	2.0±0.5
RAP	0.9
OTTO FUEL II	1.4±1.6
PNJ for TOW	1.66

---

are double base propellants, produced by both solvent and solventless processes. 2-nitrodiphenylamine is in current use at Radford AAP, and has been used at Badger AAP and Sunflower AAP when they were in operation.

2-nitrodiphenylamine stabilizes the propellants by reacting with NO and NO<sub>2</sub> formed by degradation of nitrate esters. The reaction products

formed are N-nitrosodinitrodiphenylamines, dinitrodiphenylamines and N-nitrosodinitrodiphenylamines (Richardson, 1975).

## 2. Quantities Used

### a. Historical Use

During the period 1968-1977, Radford AAP purchased an average of 69,200 lbs of 2-nitrodiphenylamine annually. Production statistics for this period indicate that about 90% of the 2-nitrodiphenylamine in propellants was used for solventless double base propellants, predominantly the N-5 and NOSIH-AA-6 formulations. The remainder was used in solvent process double base casting powders including the AAH, ARP and PNJ formulations. However, propellant production accounted for only 48% of the 2-nitrodiphenylamine purchased. The specific amount of 2-nitrodiphenylamine processed by RAAP during 1968-1977 is shown below (Watts, 1978):

<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
262,800	40,000	0	8,900	79,800	57,250	101,400	12,500	32,200	97,100

### b. Current Use

During 1977 the average use rate of 2-nitrodiphenylamine at Radford AAP was 4,600 lb/month. Based upon December 1977 production of propellants, the following amounts of this chemical were used:

<u>Propellant</u>	<u>Lb produced December, 1977</u>	<u>Lb 2-nitrodiphenylamine Used</u>
ARP Casting Powder	100,000	2,000
NOSIH-AM-2	44,000	880
M-36	27,000	540
N-5	134,000	<u>2,680</u>
		6,100

These figures show that in December 1977, 2-nitrodiphenylamine was consumed at about 133% of the average rate for 1977.

### c. Use at Full Mobilization

The full mobilization use rate of 2-nitrodiphenylamine is about the same as the use rate in December 1977, i.e., 6,000-7,000 lb/month. Not all of the items requiring 2-nitrodiphenylamine can be produced at the same time, as they use common facilities.

### 3. Documented or Speculated Occurrences in Air or Water

The actual concentration of 2-nitrodiphenylamine in waste streams has not been measured. Effluents containing 2-nitrodiphenylamine would be expected to derive from the following sources:

- Preparation operations including weighing, grinding or classification. Dust or particulates are collected in wet scrubbers, from which both solid wastes and contaminated effluents may be generated.
- Residues from washdown operations generate effluents which are filtered and discharged. Collected solids are transported to the burning grounds.
- Process water from manufacture of propellants by the solvent process. These effluents appear in the C-line waste water stream, the 48 inch general purpose sewer and the solvent recovery area discharges.
- Process wastes from solventless propellant manufacture. These effluents appear in the rolled powder area waste streams.

Approximately 1-6% of the double base propellants produced are lost during processing operations (Smith and Dickonson, 1974). This percentage could account for 60-360 lb/month of 2-nitrodiphenylamine in the effluents at Radford AAP. In addition, 3-5% of the 2-nitrodiphenylamine handled may be lost during preparation operations. Thus, the total amount of 2-nitrodiphenylamine in waste streams may be 240-670 lb/month. This figure is also applicable to full mobilization operations.

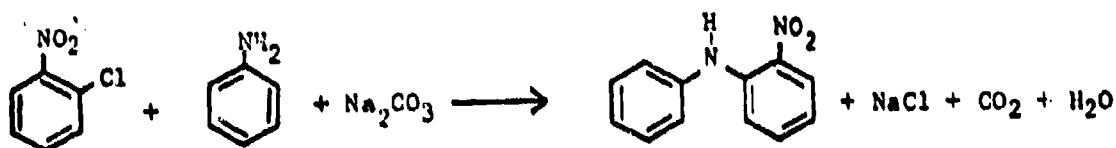
2-nitrodiphenylamine is sparingly soluble in water. Thus, much of the lost material may be recovered as solids in the effluent stream filters. The amount actually reaching the New River as a solute in effluent streams is estimated at 1/3 to 1/2 the total lost, or 80 to 200 lb/month. The presence of 2-nitrodiphenylamine has been detected in sediment samples from the New River bottom. Near outfall 22, core samples were found to contain from <0.5 to 12.2 mg/kg of 2-nitrodiphenylamine (Glennon, 1977).

#### E. Uses in the Civilian Community

##### 1. Production Methodology

2-nitrodiphenylamine can be produced on an industrial scale by reacting ortho-nitrochlorobenzene with aniline in the presence of anhydrous sodium carbonate powder.





Excess aniline is used for the reaction medium. The water which forms is removed as an aniline:water azeotrope. The reaction runs for nine hours. 2-nitrodiphenylamine is recovered by washing and recrystallization. The yield is 96% (Desseigne and Rubussier, 1957).

## 2. Manufacturers, Production, and Capacities

The only U.S. producer of 2-nitrodiphenylamine is the American Cyanamid Co. They operate a plant of unknown capacity in Marietta, Ohio (S.R.I., 1977). 2-nitrodiphenylamine is manufactured exclusively for sale (American Cyanamid, 1977a). Historical production statistics are unavailable due to their proprietary nature.

## 3. Usages

The only civilian use for 2-nitrodiphenylamine is as a chemical intermediate in the dye industry.

## 4. Future Trends

No future applications for 2-nitrodiphenylamine in the civilian sector are anticipated.

## 5. Speculated or Documented Occurrences in the Environment

Occurrences of 2-nitrodiphenylamine in the environment from civilian production or use have not been reported.

## F. Comparison of Military and Civilian Uses and Pollution of 2-nitrodiphenylamine

Since American Cyanamid is the only U.S. producer of 2-nitrodiphenylamine, it is not possible to obtain production statistics. From Radford purchases, production capacity of 2-nitrodiphenylamine must be >250,000 lb/yr. The amount of sales to the dye industry is also not available. However, it appears that the Army is one of the main users of 2-nitrodiphenylamine and probably one of the major polluters as well.

## G. Toxicological and Environmental Hazards

### 1. Toxicity to Mammals

Only limited toxicological studies with 2-nitrodiphenylamine have been conducted. The oral LD50 of 2-nitrodiphenylamine for rats is 6.15 g/kg (American Cyanamid, 1977). A 24 hour LD50 for skin contact in rabbits was determined to be >10 g/kg. American Cyanamid (1977b) did not observe any

irritation when 2-nitrodiphenylamine was applied to rabbit eyes or skin. This data indicates 2-nitrodiphenylamine has a low toxicity.

## 2. Toxicity to Aquatic Organisms

Levels of 2-nitrodiphenylamine in the aquatic environment have received little attention. Weitzel *et al.* (1976) found 2-nitrodiphenylamine levels in the sediment in the New River ranged from 0.5-12.2 ppm with a mean of about 1.5 ppm. These levels are low due to losses in the analytical procedure. Warner *et al.* (1978) determined the acute toxicity of 2-nitrodiphenylamine to aquatic organisms (Table V-3). They found 2-nitrodiphenylamine was most toxic to *Daphnia magna*. Their study indicates that 2-nitrodiphenylamine and diphenylamine have a similar toxicity.

Radford AAP currently uses 6000-7000 lb/month of 2-nitrodiphenylamine. This use rate is approximately the same as it would be at full mobilization. It has been estimated that 80 to 200 lb/month would be released into New River. Table V-4 shows the concentrations of 2-nitrodiphenylamine that could occur at different flow rates and mixing percentages. From these data, 2-nitrodiphenylamine can be toxic to aquatic organisms in a limited area of the river. Data from Weitzel *et al.* (1976) substantiates our estimates. They found effluent water levels of 2-nitrodiphenylamine ranged from 1-14 ppm, with a mean of 3.5 ppm. If the effluent mixes with 10% of the river flow, the concentration of 2-nitrodiphenylamine is approximately 40 ppb.

Upon release into New River, 2-nitrodiphenylamine would probably react in a similar way as diphenylamine. 2-nitrodiphenylamine would build up in the sediment and undergo various nitration reactions. 2-nitrodiphenylamine could be degraded to amino-diphenylamine which has a greater toxicity (Weitzel *et al.*, 1976). Other problems could occur with various 2-nitrodiphenylamine derivatives and their toxicity to aquatic organisms.

## 3. Toxicity to Microorganisms and Plants

No data was retrieved on the toxicity of 2-nitrodiphenylamine to microorganisms or plants.

## 4. Availability of Literature for Phase II

The only toxicological data on 2-nitrodiphenylamine obtained was from the manufacturer's data sheet and U. S. Army Medical Research and Development Command-sponsored studies. Information for a Phase II study would have to come from the manufacturer and foreign literature.

## H. Standards and Regulations

There are no specific United States' standards or regulations for 2-nitrodiphenylamine. This compound is listed in EPA's "Toxic Substances Control Act Test of Candidate Chemical Substances;" however, EPA does not

Table V-3. Acute Toxicity to Aquatic Organisms of  
2-nitrodiphenylamine.

<u>Species</u>	<u>Hours</u>	<u>LC50 (ppm)</u>	<u>Reference</u>
<i>Daphnia magna</i>	24	<1.8	Warner <i>et al.</i>
"	48	1.2	"
Fathead Minnow	24	3.85	"
( <i>Pimephales promelas</i> )	48	<3.85	"
"	96	2.14	"
Green Sunfish	96	<5.86	"
( <i>Lepomis cyanellus</i> )			

Table V-4. 2-nitrodiphenylamine Levels (ppm) in New River  
at Full Mobilization.\*

<u>Degree of mixing</u>	<u>Low Flow (336 mgd)</u>	<u>Average Flow (2500 mgd)</u>
1X	0.22	0.03
10X	0.022	0.003
100X	0.0022	0.0003

\*based on losses of 200 lb/month

have any plans for further studies on this compound in the near future.

#### I. Conclusions and Recommendations

The goal of this preliminary problem definition study on 2-nitrodiphenylamine was to assess the Army's responsibility for sponsoring further studies on this chemical. From the information gathered during this study, the following conclusions can be drawn:

1. Although 2-nitrodiphenylamine is not a militarily unique chemical, the Army's propellant production is the major user and polluter of the chemical.

2. Although this compound is relatively non-toxic to mammals, it is highly toxic to aquatic organisms. Any discharge represents a serious environmental hazard.

On the basis of the results for this preliminary study, it is recommended that 2-nitrodiphenylamine be included in the detailed Phase II evaluation. If sufficient information is not available in the foreign or older literature on the environmental fate of 2-nitrodiphenylamine, laboratory studies should be conducted to determine:

- Microbial transformation of this compound.
- The ability of the planned treatment processes to effectively remove the compound from the waste streams.
- The toxicity and environmental fate of degradation products.

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AD

**PRELIMINARY PROBLEM DEFINITION STUDY OF  
48 MUNITIONS-RELATED CHEMICALS**

**VOLUME II PROPELLANT RELATED CHEMICALS**

**N-NITROSODIPHENYLAMINE**

**FINAL REPORT**

**J. F. Kitchens  
W. E. Harward III  
D. M. Lauter  
R. S. Wentzel  
R. S. Valentine**

**April 1978**

**Supported by:**

**U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND  
Fort Detrick, Frederick, Maryland 21701**

**Contract No. DAMD17-77-C-7057**

**COTR: Clarence Wade, Ph.D.**

**ATLANTIC RESEARCH CORPORATION  
Alexandria, Virginia 22314**

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**The findings in this report are not to be construed as an  
official Department of the Army position unless so design-  
ated by other authorized documents.**

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## SUMMARY

N-nitrosodiphenylamine is not used by the Army in its munitions production. This compound is formed in solid propellants as a result of the reaction of diphenylamine with NO. The NO is produced from the degradation of nitrate ester explosives in the propellant. N-nitrosodiphenylamine is present in the effluents from propellant manufacture. Maximum discharges of this compound at full mobilization are estimated to be 360-600 lb/year. However, it could be formed in the environment by the action of micro-organisms. Studies have indicated that N-nitrosamine can be formed microbially from diphenylamine and nitrate.

N-nitrosodiphenylamine is produced commercially by four companies. Its only use is as a vulcanization retarder for rubber. However, N-nitrosodiphenylamine is being replaced by steroid-type retarders by the rubber industry.

The toxicity of N-nitrosodiphenylamine in acute doses is low (LD50 for rats is 5360 mg/kg). This compound has been tested for its carcinogenic potential. It has been found to be non-carcinogenic. The aquatic toxicity of this compound is unknown.

From the information evaluated in this study, it is concluded that N-nitrosodiphenylamine is not a military unique chemical. Any potential effects of this compound on the aquatic ecosystem would be overshadowed by those of diphenylamine. Therefore N-nitrosodiphenylamine should be a low priority chemical for further study by the Army.

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## FOREWORD

This report details the results of a preliminary problem definition study on N-nitrosodiphenylamine. The purpose of this study was to determine the Army's responsibility for conducting further research on N-nitrosodiphenylamine in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on N-nitrosodiphenylamine, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

N-nitrosodiphenylamine was only one of the 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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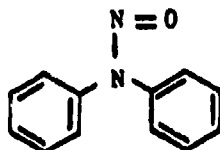
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## VI. N-nitrosodiphenylamine

### A. Alternate Names

N-nitrosodiphenylamine is a nitrosamine having the following structure:



The molecular formula of this compound is  $C_{12}H_{10}N_2O$  corresponding to a molecular weight of 198.23 g/mole. Alternate names for N-nitrosodiphenylamine are listed below:

CAS Registry No.:	86-30-6
CA Name (9 CI):	Benzenamine, N-nitroso-N-phenyl-
CA Name (8 CI):	Diphenylamine, N-nitroso-
Wiswesser Line Notation:	ONNR&R
Synonyms:	Diphenylnitrosamine; N-nitroso-N-phenylaniline; N-nitroso-diphenylamine; Nitrosodiphenylamine; Redax, Retarder J; Vulcatard A; Vulkalent A; Vultrol

### B. Physical Properties

The physical properties of N-nitrosodiphenylamine are presented in Table VI-1. The infrared spectra of N-nitrosodiphenylamine shows absorption at 3050, 1590, 1490, 1480, 1440, 1300, 1180, 1150, 1080, 1040, 990, 900, 750, 740 and 690  $cm^{-1}$  (CRC, 1974). The ultraviolet spectra of the compound in ethanol has an absorption maximum at 290 nm (Davidson, 1974).

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Table VI-1. Physical Properties of N-nitrosodiphenylamine.

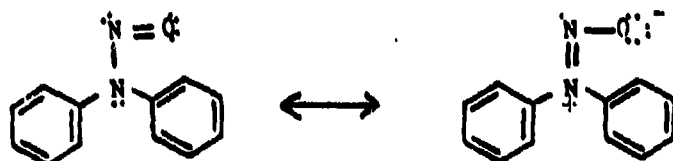
Physical Form @ 20°C:	solid
Color and Crystal Form:	yellow to brown or orange powder or flakes
Odor:	mildly amine
M.P.:	64-66°C
Specific Gravity:	1.23
Solubility:	water - practically insoluble. Soluble in acetone, benzene, alcohol and ethylene dichloride. Somewhat soluble in gasoline

\*References: Hawley, 1977; American Cyanamid Company, 1974.

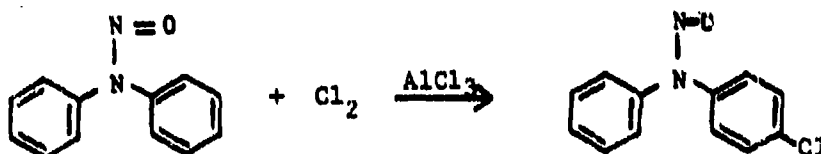
## C. Chemical Properties

### 1. General Reactions

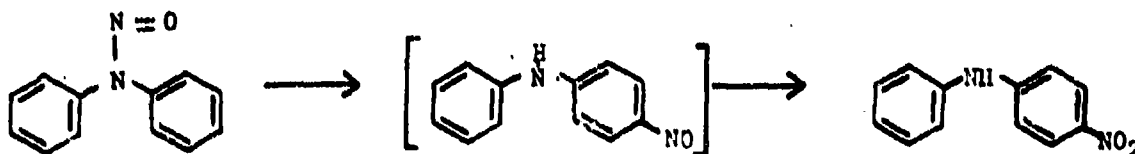
N-nitrosodiphenylamine, like other aromatic compounds, will undergo electrophilic substitution on the aromatic ring. Its reactivity is comparable to benzene due to the delocalization of the amino unshared electron pair to the nitroso function.



Halogenation will occur in the presence of a catalyst.

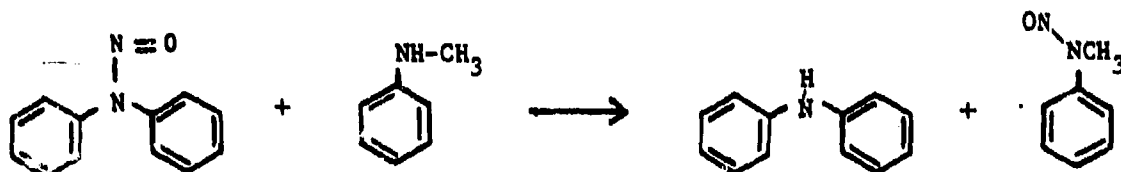


Direct nitration does not occur. In the presence of nitric acid, N-nitrosodiphenylamine undergoes the Fischer-Hepp rearrangement to C-nitrosodiphenylamine which is immediately oxidized to C-nitrodiphenylamine. Migration of the nitroso group to the para position of the ring predominates.



In aqueous HCl the rearrangement occurs without subsequent oxidation.

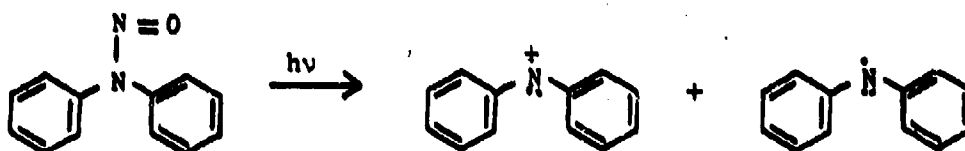
N-nitrosodiphenylamine readily acts as a donor of the nitroso group. Transnitrosation between N-nitrosodiphenylamine and N-methylaniline occurs at normal temperatures in dilute acid.



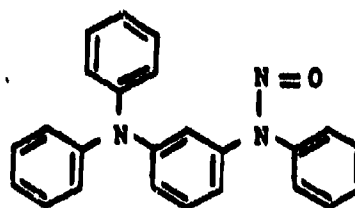
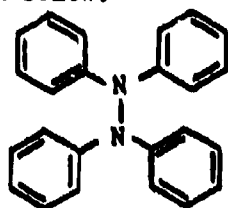
Kinetic studies indicate that the reaction is a direct transfer of the nitroso group rather than transfer proceeding via free nitrous acid (Challis and Osborne, 1972).

## 2. Environmental Reactions

The photolysis of N-nitrosodiphenylamine in an organic solvent at low temperatures has been investigated. Irradiation at 250 to 300 nm produces two species (Lewis and Lipkin, 1942).



These products may undergo a number of possible reactions including radical coupling and electrophilic substitution to form compounds similar to those shown below.



## 3. Sampling and Analysis

N-nitrosodiphenylamine may be analysed by several methods including gas chromatography, ultraviolet spectroscopy and thin layer chromatography. However, analytical results vary significantly depending on the care taken in the purity of solvents, preparatory procedures and exposure to light. If the solvents are impure or the solutions are exposed to light, denitrosation rapidly occurs changing the analytical results (Davidson, 1974). Denitrosation also occurs in the gas chromatography. This denitrosation is reproducible, but not stoichiometric. The presence of diphenylamine is a significant interference in all analytical methods and its presence must be quantitated in order to assess the amount of N-nitrosodiphenylamine present in the sample.

## D. Uses in Army Munitions

### 1. Purposes

N-nitrosodiphenylamine is not a component in the formulation of propellants. It is a degradation product of diphenylamine, which appears as the propellant ages. The ratio of N-nitrosodiphenylamine to diphenylamine in the propellant is used as a measure of the quality of the propellant (Richardson, 1975).

N-nitrosodiphenylamine is formed when diphenylamine reacts with NO produced from degradation of nitrate esters. The N-nitrosodiphenylamine also acts as a stabilizer. This compound further reacts with NO or NO<sub>2</sub> to form nitrodiphenylamines and N-nitrosodiphenylamines (Richardson, 1975).

## 2. Quantities Used

Since N-nitrosodiphenylamine appears only as a degradation product, only very small amounts would be expected to appear during the propellant manufacturing process. It is anticipated that a maximum of 1% of the diphenylamine lost is converted to N-nitrosodiphenylamine. This conversion rate would account for 3 to 5 lb/month at current production rates and 30 to 50 lb/month at full mobilization rates.

## 3. Documented or Speculated Occurrences in Air or Water

N-nitrosodiphenylamine would appear in any effluent stream which receives diphenylamine. Since diphenylamine is used for single base propellants made by the solvent process, the C-line waste streams at Radford AAP may contain some N-nitrosodiphenylamine. There has never been a quantitative measurement of this material in plant effluents, however.

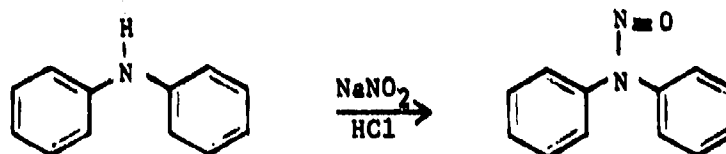
Since N-nitrosodiphenylamine is not added to the propellant formulations, there are no losses associated with chemical preparation steps. This represents a major source of losses for most propellant additives.

It is unlikely that diphenylamine is converted into N-nitrosodiphenylamine after it is leached from propellant particles and enters the effluent streams as a solute. The concentration of diphenylamine is only a few parts per million at most, so the transformation is not probable (Glennon, 1977).

## E. Uses in the Civilian Community

### 1. Production Methodology

N-nitrosodiphenylamine is produced commercially by direct nitrosation of diphenylamine (American Cyanamid, 1978).





Nitrous acid is generated *in situ* by the addition of sodium nitrite to strong acid. A non-oxidizing acid such as HCl must be used to prevent migration of the nitroso group onto the aromatic rings.

## 2. Manufacturers, Production, and Capacity

Manufacturers of N-nitrosodiphenylamine are listed in Table VI-2 (S.R.I. 1977).

---

Table VI-2. N-nitrosodiphenylamine Producers.

American Cyanamid Co., Organic Chems. Div.	Bound Brook, N.J.
The B.F. Goodrich Co., B.F. Goodrich Chem. Co. Div.	Akron, Ohio
The Goodyear Tire & Rubber Co.	Akron, Ohio
Uniroyal, Inc., Uniroyal Chem. Div.	Naugatuck, Conn.

---

American Cyanamid manufactures N-nitrosodiphenylamine for sale under the trade name Retarder 2N. B.F. Goodrich, Goodyear, and Uniroyal manufacture N-nitrosodiphenylamine for use in their rubber products. Production capacities are not available.

Table VI-3 contains the reported U.S. production of N-nitrosodiphenylamine since 1969 (U.S. Tariff Commission).

---

Table VI-3. U.S. Production<sup>1</sup> of N-nitrosodiphenylamine.

1969	1970	1971	1972	1973	1974	1975	1976
2047	1528	1660	2018	2485	3496	1680	1307

1. in thousand pounds

---

### 3. Usages

N-nitrosodiphenylamine is used exclusively as a vulcanization retarder in the rubber processing industry.

### 4. Future Trends

N-nitrosodiphenylamine is being replaced in the rubber industry by steroid-type retarders. This phasing out is due to concern over N-nitrosodiphenylamine's toxicity and possible carcinogenicity (Salisbury Labs, 1978).

### 5. Documented or Speculated Occurrences in the Environment

There are no reports of N-nitrosodiphenylamine in the civilian environment from civilian manufacture or use.

### F. Comparison of Military and Civilian Uses of N-nitrosodiphenylamine

The military does not intentionally produce N-nitrosodiphenylamine in its propellant manufacturing facilities. This compound is a by-product formed by the reaction of the diphenylamine stabilizer with NO produced by degradation of nitrate esters. Maximum environmental discharge of this compound would be ~ 30-50 lb/month or 360-600 lb/year from each operating plant at full production capacity. Thus the maximum military discharge at full mobilization of Radford, Badger and Sunflower would be 1800 lb/year.

N-nitrosodiphenylamine is produced by the civilian community as a rubber stabilizer. Over 1 million pounds are produced annually in the United States. Although no figures are available for environmental discharges from civilian production and usage of N-nitrosodiphenylamine, a 1% loss would not be unreasonable. Based on 1976 production rates, a 1% loss would result in an environmental discharge of 13,070 lb/year. The projected maximum military discharge is only 14% of the present civilian discharge of N-nitrosodiphenylamine. Current military discharges are only 0.5% that of the civilian community.

Thus, N-nitrosodiphenylamine is not a military unique chemical at this point in time. However, in the future it may be a military unique compound due to the replacement of N-nitrosodiphenylamine by other compounds in the rubber industry.

### G. Environmental and Toxicological Hazards of N-nitrosodiphenylamine

#### 1. Mammalian Toxicity

The acute toxicity of N-nitrosodiphenylamine has been determined in the rabbit and mouse by oral administration and skin contact. The resulting data are compiled in Table VI-4.

Table VI-4. Acute Toxicity of N-nitrosodiphenylamine to Mammals.

Species	Route of Administration	Dose mg/kg	Effect	Reference
Mouse	Skin Contact	1000	TDLo	Bionetics Research Lab.
Mouse	Oral	410	TDLo	"
Albino rat	Oral	5360	LD50	American Cyanamid Company, 1974
Albino rat	on clipped skin	>5000	24 hr LD50	"

Inspection of the Table indicates that N-nitrosodiphenylamine has a low toxicity. No irritation was observed when N-nitrosodiphenylamine was applied to rabbit eyes or skin.

N-nitrosodiphenylamine has been tested for carcinogenic potency. It is considered noncarcinogenic and is thus one of the few N-nitroso compounds which does not produce cancer.

## 2. Aquatic Toxicity

No literature concerning the aquatic toxicity of N-nitrosodiphenylamine was retrieved. However, due to the low mammalian toxicity combined with the limited water solubility and limited lifetime of N-nitrosodiphenylamine, this compound should present little toxicity to aquatic organisms unless released in massive amounts.

## 3. Toxicity to Microorganisms

Little if any research has been conducted on the growth inhibition or toxicity of N-nitrosodiphenylamine to bacteria. However, N-nitrosodiphenylamine can be degraded by microorganisms. The percent breakdown of N-nitrosodiphenylamine by several bacteria is shown in Table VI-5. As seen in the Table, *Streptococcus faecalis* strains consistently metabolize N-nitrosodiphenylamine. Rowland and Grasso (1975) also observed that the lower the concentration of N-nitrosodiphenylamine the more efficient the degradation. Nitrate ion and diphenylamine are the products of the degradation.

While more information about N-nitrosodiphenylamine is needed, it is apparent from this data that N-nitrosodiphenylamine is degradable. Thus a low release should not be highly toxic to microorganisms.

Table VI-5. Microbial Degradation of N-nitrosodiphenylamine  
(Rowland and Grasso, 1975)

<u>Bacterium</u>	<u>Strains Tested</u>	<u>Percent Positive Breakdown</u>
bacteroids	7	29
bifidobacterium	6	33
<i>Escherichia coli</i>	25	76
Lactobacillus	15	73
<i>Streptococcus faecalis</i>	14	93

#### 4. Phytotoxicity

No information was retrieved on the phytotoxicity of N-nitrosodiphenylamine.

#### 5. Environmental Fate

N-nitrosodiphenylamine has been shown to rapidly degrade to diphenylamine in the presence of light. (Davidson, 1974). It is also degraded to diphenylamine by microorganisms (Rowland and Grasso, 1975). Thus, it appears that any environmental effects would be from diphenylamine and its potential reaction products. Since diphenylamine is released at Radford AAP at much higher levels than N-nitrosodiphenylamine, its environmental hazards could overwhelm any hazards from N-nitrosodiphenylamine.

#### 6. Literature Availability for Phase II

Several studies have been performed or are being performed on the toxicological properties of N-nitrosodiphenylamine. There should be sufficient literature available for a Phase II toxicological evaluation. Environmental data is not as plentiful, however contacts with manufacturers (especially their pollution abatement personnel) may lead to more information.

#### H. Regulations and Standards

##### 1. Air and Water Regulations

No specific air and water discharge regulations are in effect for N-nitrosodiphenylamine. However, EPA has proposed effluent guideline

standards for the rubber processing point source category. N-nitrosodiphenylamine would come into this effluent standard (Federal Register, January 10, 1975).

## 2. Health Standards

No threshold limit values have been set for N-nitrosodiphenylamine. It is listed on EPA Toxic Substances Control Act Candidate List of Chemical Substances (1977). NCI (1978) has studied N-nitrosodiphenylamine in its carcinogenic program, however, this report is not yet available.

## I. Conclusions and Recommendations

In this preliminary problem definition study report, the civilian and military usage and pollution associated with N-nitrosodiphenylamine has been examined. On the basis of this information, it is concluded that N-nitrosodiphenylamine is not a military unique compound. It does not appear to be highly toxic or carcinogenic to mammals. Although the aquatic toxicity of this compound is unknown, any toxic effects would be overshadowed by the more prevalent highly toxic diphenylamine. Therefore it is recommended that the Army not initiate any further work on this compound. However it may enter into a study of the environmental fate of diphenylamine.

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PRELIMINARY PROBLEM DEFINITION STUDY OF  
48 MUNITIONS-RELATED CHEMICALS

VOLUME II PROPELLANT RELATED CHEMICALS

THE PHTHALATE ESTERS

FINAL REPORT

J. F. Kitchens  
W. E. Harvard III  
D. M. Lauter  
R. S. Wentzel  
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND  
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION  
Alexandria, Virginia 22314

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official Department of the Army position unless so design-  
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## SUMMARY

Diethyl-, dibutyl- and diethylhexyl phthalate are used as plasticizers in the manufacture of solid propellants at Radford, Badger, Sunflower and Indiana Army Ammunition Plants. Currently, only Radford and Indiana are operational. Of the phthalate esters, dibutyl phthalate is the largest volume propellant additive. At current production rates, Radford uses 344,400 lb/year of this compound, primarily for the M-1 formulation. At full mobilization, 2.5 million lb/year of dibutyl phthalate would be needed by Radford AAP alone. Estimated discharges of dibutyl phthalate to the New River at full mobilization are 1040 to 4160 lb/month.

Diethylphthalate is used exclusively in the N-5 and M-8 propellant formulations. Current use rate of diethyl phthalate is 228,000 lb/year. Radford is currently operating at full production capacity of these propellants. Discharge of diethyl phthalate to the New River is estimated at 95 to 380 lb/month.

Diethylhexyl phthalate is seldom used by Radford. Only 22,000 lb of this chemical has been formulated into propellants over the last 10 years.

The phthalate esters are widely used throughout the civilian community. Over 1,043 million lb of phthalate esters were produced in the United States in 1976. The 1976 production of the individual esters was

- diethylhexyl phthalate	296.7 million lb
- dibutyl phthalate	13.7 million lb
- diethyl phthalate	16.1 million lb

Each of these esters is used as a plasticizer for different materials. Diethylhexyl phthalate is used in PVC plastic; dibutyl phthalate in nitro-cellulose and polyvinyl acetate emulsions and diethyl phthalate in cellulose acetate plastics.

The acute toxicity of the phthalate esters to mammals is low with LD50's ranging from 1 to 8 g/kg. Some subtle biochemical changes are observed in mammals exposed to phthalate esters over long periods of time. The esters have been shown to be noncarcinogenic. However, they have mutagenic and teratogenic potential in high doses.

The phthalate esters are widespread throughout the environment. They are found in river and ocean water, sediment and biota. Diethylhexyl phthalate is the most abundant of the phthalate esters in the environment. The phthalate esters are fairly toxic to aquatic organisms with 96 hour LC50s in the low ppm. Some bioaccumulation of these compounds occurs; however, they are actively metabolized by most organisms. Microorganism degradation of diethyl- and dibutyl- phthalate occurs rapidly under aerobic conditions. Degradation of diethylhexyl phthalate is slow.

From the information evaluated during this study, it is concluded that the phthalate esters are not military unique chemicals. Dibutyl phthalate appears to be the most widely used phthalate ester by the military. At current propellant production rates, the military use of this chemical is only a small percentage of the civilian production. However, if all four propellant plants were operating at full mobilization levels, military use of dibutyl phthalate could be as high as 73% of the 1976 civilian production of this chemical. Dibutyl phthalate discharges would be as high as 4160 lb/month from Radford AAP at full mobilization. At this discharge level, this chemical would be toxic to aquatic life. Further evaluation of the environmental fate of dibutyl phthalate by the Army may be warranted. However, the proposed biotreatment facility should adequately remove this compound from Radford's effluents. Thus, this chemical should be a low priority for further study.

Diethyl phthalate is not used or discharged in amounts harmful to the environment. It is also a relatively low use chemical in propellant manufacture. Based on these facts and the ease with which diethyl phthalate is biodegraded, this chemical should be a low priority for further study.

The Army's utilization of diethylhexyl phthalate is insignificant when compared to that of the civilian community. Therefore, diethylhexyl phthalate should be a low priority chemical for further study by the Army.

## FOREWORD

This report details the results of a preliminary problem definition study on phthalate esters. The purpose of this study was to determine the Army's responsibility for conducting further research on phthalate esters in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on phthalate esters, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Phthalate esters was only one of the 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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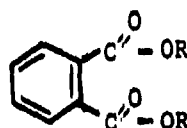
## VII. PHTHALATE ESTERS

### A. Introduction

The Army used several phthalate esters as plasticizers in the manufacture of propellants and other products. Dibutyl- and diethyl phthalate are consistently used in relatively large volumes. Diethylhexyl phthalate is also used by the Army on occasion.

### B. Alternate Names

The phthalate esters of concern to the Army are the diesters of o-phthalic acid having the following general structure formula



where R = ethyl -  $\text{CH}_2\text{-CH}_3$

butyl -  $(\text{CH}_2)_3\text{CH}_3$

ethylhexyl -  $\text{CH}_2\text{-CH}(\text{CH}_2\text{-CH}_3)(\text{CH}_2)_3\text{-CH}_3$

The pertinent alternate names for these compounds are listed below:

#### Diethyl phthalate

Molecular Formula:	$\text{C}_{12}\text{H}_{14}\text{O}_4$
Molecular Weight:	222.24 g/mole
CAS Registry No.:	84-66-2
CA Name (9CI):	1,2-benzenedicarboxylic acid, diethyl ester
CA Name (8CI):	Phthalic acid, diethyl ester
Wiswesser Line Notation:	20VR BV02
Synonyms:	Anozol; o-benzenedicarboxylic acid, diethyl ester; Diethyl phthalate; Ethyl phthalate; Neantine; Palatinol A; Phthalol; Placidol E; Solvanol; Unimoll DA

#### Dibutyl phthalate

Molecular Formula:	$\text{C}_{16}\text{H}_{22}\text{O}_4$
Molecular Weight:	278.35

CAS Registry No.:	84-74-2
CA Name (9CI):	1,2-benzenedicarboxylic acid, dibutyl ester
CA Name (8CI):	Phthalic acid, dibutyl ester
Wiswesser Line Notation:	40VR BV04
Synonyms:	Butyl phthalate; Celluflex DPB; Dibutyl phthalate; Elaol; Genoplast; Hexaplas M/B; n-butyl phthalate; Palatinol C; Polycizer DBP; PX 104; Staflex DBP; Unimoll DB; Witcizer 300

Diethylhexylphthalate

Molecular Formula:	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>
Molecular Weight:	390.56
CAS Registry No.:	117-81-7
Replaces CAS Registry Nos.:	8033-53-2; 40120-69-2; 50885-87-3
CA Name (9CI):	1,2-benzenedicarboxylic acid, bis(2-ethylhexyl) ester
CA Name (8CI):	Phthalic acid, bis(2-ethylhexyl) ester
Wiswesser Line Notation:	4Y2&1OV 2 BR
Synonyms:	bis(2-ethylhexyl)-1,2-benzenedicarboxylate; bis(2-ethylhexyl) phthalate; Bisoflex 81; Compound 88 DEHP; Di-(ethylhexyl) phthalate; Di-(2-ethylhexyl)-phthalate; Diethylhexyl phthalate; Dioctyl phthalate; DOP; Ethylhexyl phthalate; 2-ethylhexyl phthalate; Fleximel; Flexol DOP; Kodaflex; Octoil; Octyl phthalate; Palatinol AH; Phthalic acid dioctyl ester; Pittsburgh PX-138; Sicol 150; Staflex DOP; Truflex DOP; Vestinol AH; Witcizer 312

C. Physical Properties

The physical properties of diethyl-, dibutyl- and diethylhexylphthalate are presented in Table VII-1.

The infrared spectra of diethyl- (DEP), and dibutyl phthalate (DBP) and dioctyl or diethylhexylphthalate (DEHP) are shown in Figure VII-1. There is some confusion in the literature on the infrared spectra of diethylhexylphthalate. The older literature uses the names dioctylphthalate and diethyl-

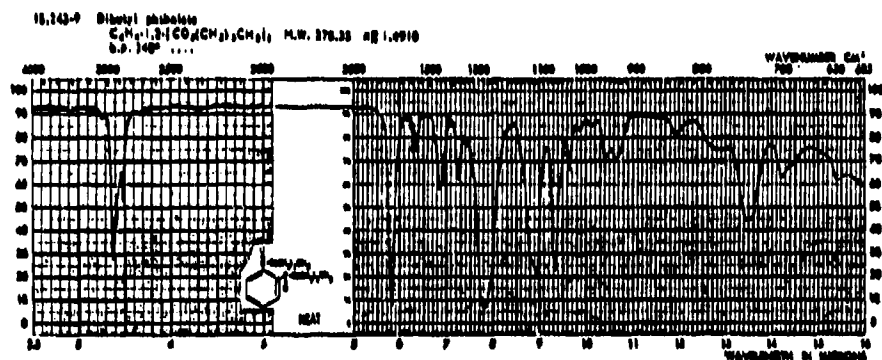
Table VII-1. Physical Properties of the Phthalate Esters\*.

	<u>Diethyl phthalate</u>	<u>Dibutyl phthalate</u>	<u>Diethylhexyl phthalate</u>
Physical Form @ 20°C:	oily liquid	oily liquid	liquid
Color:	colorless	colorless	light colored
Odor:	slightly aromatic	mild	odorless
B.P.:	298.5°C @ 760 mmHg	339°C @ 760 mmHg	350°C @ 760 mmHg 231°C @ 5 mmHg
M.P.:	<-50°C	-40°C	
Vapor Pressure:	100 mmHg @ 220°C 1.0 mmHg @ 109°C	0.0001 mmHg @ 25°C 0.8 mmHg @ 150°C 14.0 mmHg @ 200°C 100 mmHg @ 250°C	1.32 mmHg @ 200°C 18.0 mmHg @ 250°C
Vapor Density (air=1):	7.66		216°C (COC)
Flash Point:	161°C (COC)	182°C (COC)	
Flammability Limits in Air:	0.75Z (vol) @ 187°C		
Specific Gravity @ $\frac{25}{25}^{\circ}\text{C}$ :	1.120	1.045	0.983
Refractive Index, $n_D^{25}$ :	1.4990	1.4925	1.4836
Viscosity, Cp:	34.8 @ 9°C 21 @ 20°C 9.5 @ 25°C 1.7 @ 100°C	20 @ 20°C	81.4 @ 20°C
Solubility	water - 0.012 g/100g	water - 0.001 g/100g	water <25 ppm miscible with mineral oil

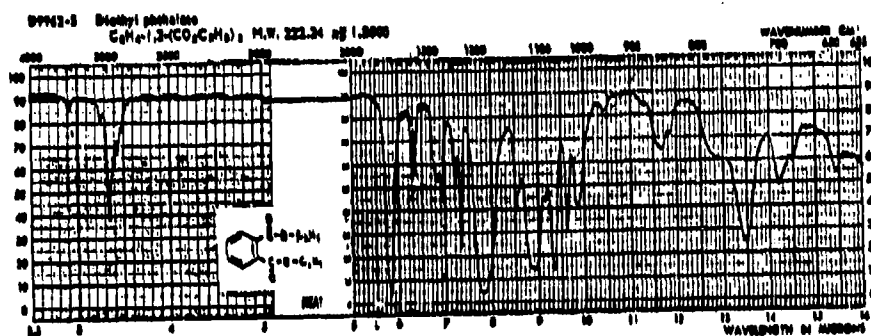
\* References: Hawley, 1977; Eastman Chemical Products, Inc., 1976; W. R. Grace &amp; Co.; Peakall, 1975.



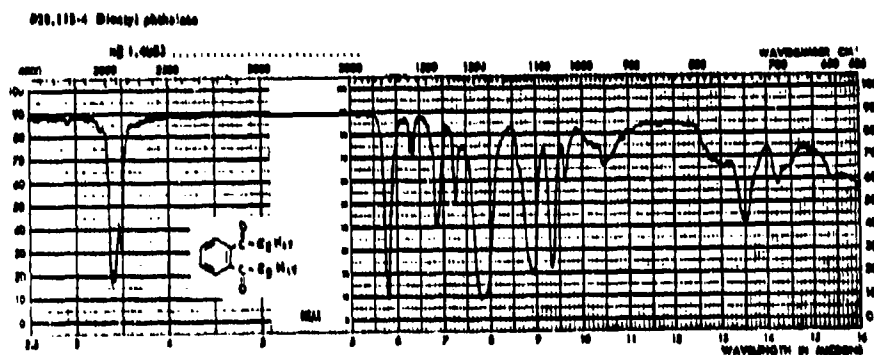
Figure VII-1. Infrared Spectra of the Phthalate Esters.  
(Pouchert, 1970)



Dibutyl Phthalate



Diethyl Phthalate



Dioctyl Phthalate

hexyl phthalate interchangeably. CRC (1974) lists two infrared spectra, the one shown in Figure VII-1 and the following:

**Absorption bands at**

3070, 3020, 2930, 2890, 2860, 2720, 2580, 1720, 1590, 1570, 1480, 1440, 1380, 1260, 1150, 1110, 1030, 950, 880, 850, 820, 750, 640, 390, 230  $\text{cm}^{-1}$

The latter spectra is probably the correct one.

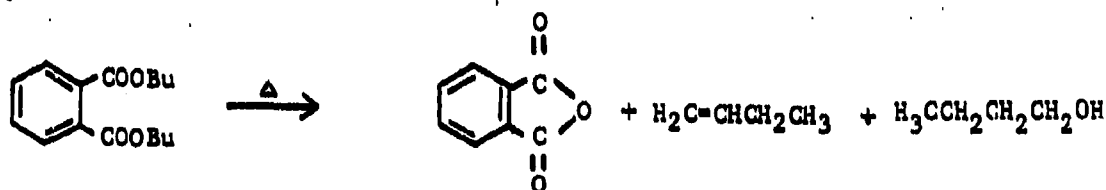
The ultraviolet spectra of diethylphthalate in methanol has two absorption bands. The wavelengths of absorption maxima are 274 and 225 nm with molar absorptivity coefficients of 1270 and 8310 respectively (CRC, 1974). The ultraviolet spectra of dibutyl phthalate in methanol is similar (CRC, 1974):

$\lambda_{\text{max}} = 274 \text{ nm}, \epsilon = 1230$   
 $\lambda_{\text{max}} = 225 \text{ nm}, \epsilon = 7960$

**D. Chemical Properties**

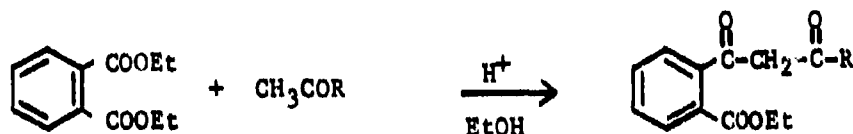
**1. General Reactions**

Pyrolysis of DBP via distillation yields phthalic anhydride and equivalent amounts of butene and butanol.

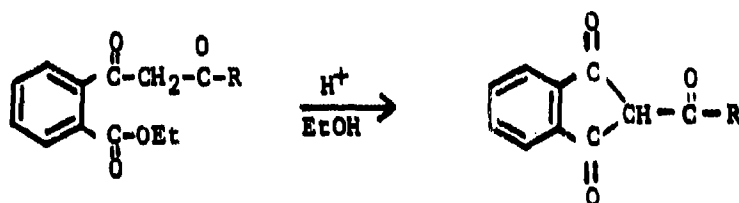


The presence of acids or PVC catalyze the thermal degradation of phthalate esters. Heating of DEHP at  $170^\circ\text{C}$  for 40 hours in the presence of  $\text{H}_2\text{SO}_4$  or PVC yields phthalic anhydride and 3-methylheptene and its isomerization products. No alcohol was found. Isobutene, butene, and propylene were formed from pyrolysis of dibutyl phthalate at  $730^\circ\text{C}$  with a hot wire (Fishbein and Albro, 1972).

Phthalate esters are easily converted into a bicyclic ring system. Reaction with an "activated" methyl group gives a non-isolable first formed product.



The methyl group acts as a nucleophile because it is adjacent to the carbonyl function. It is said to be 'activated'. In the product formed, the methylene carbon is adjacent to both its original carbonyl and a phthalate carbonyl. It is now doubly activated. Under the reaction conditions, this product will behave as a stronger nucleophile than the starting materials. Nucleophilic substitution will occur at the remaining ester function.

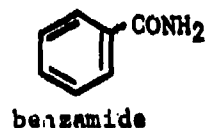
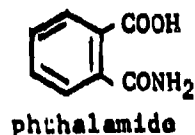


Carboxylate substituents on an aromatic ring decrease the ring's susceptibility toward electrophilic substitution. Substitution on the phthalate ring would be difficult and slow, but would occur at the 4 position.



## 2. Environmental Reactions

Hydrolysis of esters is readily catalyzed by either acid or bases. Phthalate esters are hydrolyzed to phthalic acid (or phthalate anion in base) rather than the monoester. The rate of hydrolysis of the monoester is greatly enhanced over the diester by the presence of the free acid function. This rate enhancement is seen in the hydrolysis of other derivatives of phthalic acid. For example, the rate of hydrolysis of phthalamide is  $10^5$  times faster than the hydrolysis of benzamide (March, 1968).



### 3. Sampling and Analysis

Many sampling and analysis procedures have been proposed for determination of the phthalate esters in air, water, blood and tissue samples. Thin layer chromatography is often employed to separate and identify the phthalate esters. Methylene chloride or ethyl ether extracts of samples of phthalate esters can be separated and identified by chromatographing on a Silica Gel plate. Development is accomplished by  $\text{SbCl}_5$  in chloroform or resorcinol- $\text{ZnCl}_2$ - $\text{H}_2\text{SO}_4$  reagent (Fishbein and Albro, 1972).

Phthalates in air have been collected on a deactivated Florisil column. The column is eluted with petroleum ether, then ethyl ether. The ether sample is then quantitated using a gas chromatograph with an electron capture detector and a column containing 3% SE-30 on the appropriate support. Low levels ( $\text{ng}/\text{m}^3$ ) of phthalate esters in air are detectable with this procedure (Giam et al., 1975).

A similar procedure can be used to determine phthalate esters in sea water. Background levels as low as 25 ng of DBP and 50 ng of DEHP can be obtained if proper precautions are observed.

High performance liquid chromatography has also been used to determine phthalate esters. Hexane extracts are chromatographed. Detection is accomplished with an ultraviolet absorber detector at 224 nm. The absolute detector limit is 2 ng of DEHP (Mori, 1976).

Another method which has been used to some extent is derivatization. In this procedure the ester is hydrolyzed and the acid reacted with 2-chloroethylamine hydrochloride to yield N-(2-chloroethyl)phthalimide. The phthalimide extract is then quantitated by gas chromatography with an electron capture detector (Giam et al., 1976).

Analysis of phthalate esters is a difficult task due to the extra precautions which must be taken to prevent contamination. Contamination can occur from a variety of sources including solvents, glassware and filter paper.

#### E. Uses of Phthalate Esters in Army Munitions

##### 1. Purpose

Phthalate esters are used as plasticizers in propellant formulations. The most commonly used phthalate esters are DEP and DBP. These chemicals are used at all facilities which manufacture propellants: Badger AAP, Radford AAP and Indiana AAP. In addition, DEHP is sometimes used at Radford AAP, though not in current operations.

The formulations using phthalate esters are listed below:

<u>Formulation</u>	<u>Ester Used</u>	<u>% Esters in Formulation</u>
M-1	dibutyl	5.0±1.0
M-6	dibutyl	3.0±1.0
M-6+2	dibutyl	3.0±1.0
M-8	diethyl	3.0±1.5
N-5	diethyl	10.5

These formulations include single and double base propellants made by both solvent and solventless processes.

In addition to their plasticizing function, phthalate esters also reduce the propellant burning rate in proportion to their concentration. This action reduces flash when the propellant is ignited. Phthalate esters also act as waterproofing agents.

## 2. Quantities Used

### a. Historical Use

Dibutyl phthalate is the largest volume propellant additive used, with an average of 2.54 million lb/year used at Radford AAP over the period 1968-1977. About 95% of this quantity was used in the M-1 formulation.

Diethyl phthalate is used only in the solventless double base formulations M-8 and N-5. The average amount used during 1968-1977 was 171,500 lb/year. Over half this amount was used in 1968 alone, with very little used during 1970-1974. A total of 22,000 lb of DEHP was purchased by Radford AAP in the years 1968-1977. This amount was purchased and used in three years--1968, 1972 and 1973. The specific amounts of phthalate esters processed by Radford AAP during the 1968-1977 period are shown in Table VII-2.

### b. Current Use

During 1977, Radford AAP used DEP at an average rate of 19,000 lb/month. Based upon December 1977 production rates of M-8 and N-5 propellants, 15,000 lb of DEP were used during that month, or 79% of the average use rate.

The average amount of DBP used in 1977 was 28,700 lb/month. During December 1977, 817,000 lb of M-1 propellant was produced accounting for some 41,000 lb of DBP, or about 143% of the average use rate.

Table VII-2. Historical Purchases of the Phthalate Esters  
at Radford AAP (Watts, 1978)

<u>Year</u>	<u>Diethyl phthalate</u>	<u>Dibutyl phthalate</u>	<u>Diethylhexyl phthalate</u>
1968	987,100	5,376,890	6,300
1969	282,500	3,854,218	0
1970	6,000	2,570,860	0
1971	0	2,377,790	0
1972	0	2,538,160	6,300
1973	0	2,700,010	9,450
1974	6,000	3,727,418	0
1975	63,880	1,425,700	0
1976	133,360	434,000	0
1977	236,580	349,800	0

None of the other phthalate esters, dioctyl, dipropyl or diethylhexyl are in use at the present time. DEHP is used to produce single base casting propellants. The others are specified in formulations for which there is very little demand, and thus they are rarely used.

c. Use at Full Mobilization

The current use rate of DEP, i.e., 19,000 lb/month, is essentially the same as the full mobilization use rate. However, DBP use would increase from the current 28,700 lb/month to about 208,000 lb/month if full mobilization were required. During 1968 and 1969, the mobilization schedules required use of more phthalate esters than the current mobilization plan. This accounts for the purchases of these materials during those years at above the current full mobilization rate.

3. Documented or Speculated Occurrences in Air or Water

DBP has been measured in the effluents from the "water dry" process (Glennon, 1977). The indicated loss was 15 to 45 lb/month of DBP. This single source does not represent total losses, however. Effluents containing phthalate esters could be generated from any or all of the following sources:

1. Preparation operations including weighing, grinding or classification. Dust or particulates are collected in wet scrubbers, from which both solid wastes and contaminated effluents may be generated.
2. Residues from washdown operations generate effluents which are filtered and discharged. Collected solids are transported to the burning grounds.
3. Process water from manufacture of propellants by the solvent process. These effluents appear in the C-line waste water stream, the 48 inch general purpose sewer and the solvent recovery area discharges.
4. Process wastes from solventless propellant manufacture. These effluents appear in the rolled powder area waste streams.

It is estimated that 1-4% of the phthalate esters processed are lost to waste streams (Dickensen, 1978). This amount would represent a total of 290 to 1150 lb/month of the dibutyl esters. At full mobilization, the loss of dibutyl phthalate would increase to 2080 to 8320 lb/month. The full mobilization losses of DEP would be similar to current values of 190-760 lb/month.

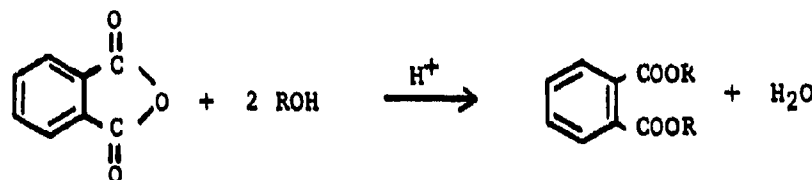
Phthalate esters are sparingly soluble in water. Thus, some of the material lost may be recovered from solids collected on effluent filters. It is probable that some phthalate esters leach out of the solids. Other

sources of loss occur from preparation operations before the phthalate esters are combined with other propellant ingredients. Thus, it is estimated that 1/2 of the total loss of phthalate esters ultimately appears in plant effluents.

## F. Uses of the Phthalate Esters in the Civilian Community

### 1. Production Methodology

Phthalate esters are prepared from phthalic anhydride and two equivalents of the appropriate alcohol, as shown in Figure VII-2. The esterification is catalyzed by acid.



The process is essentially the same for the different esters. The methodology is slightly altered to compensate for differences in the physical properties of the various alcohols. Production of DBP is typical of the phthalate esters. n-butanol and phthalic anhydride, in a 2.5:1 molar ratio, are charged into a reactor. A small amount (1% of total reaction mixture) of concentrated sulfuric acid is added as a catalyst. Toluene sulfonic acid may be substituted as the catalyst. The reactor is heated to approximately 200°C so that the water:butanol azeotrope distilling at 92°C comes off the column head. Upon cooling, this distillate separates into two layers. The aqueous layer is sent to recovery followed by disposal. The alcohol layer is returned to the column. When the maximum amount of water has been removed, the crude DBP is transferred to a vacuum column where volatile impurities are removed. Further purification can be achieved by decolorizing with activated charcoal. Yields are 90% based on anhydride used. The purity is reported at 99%.

The process is similar for the ethyl, propyl, n-octyl, and 2-ethylhexyl esters. In DEP production, benzene is introduced to the column to reduce the partial pressure of the alcohol. Water is removed as the ternary water:benzene:ethanol azeotrope (Lowenheim and Moran, 1975).

### 2. Manufacturers, Production, and Capacity

The manufacturers and plant sites of n-butyl, ethyl, and ethylhexyl phthalate diesters are listed in Table VII-3.



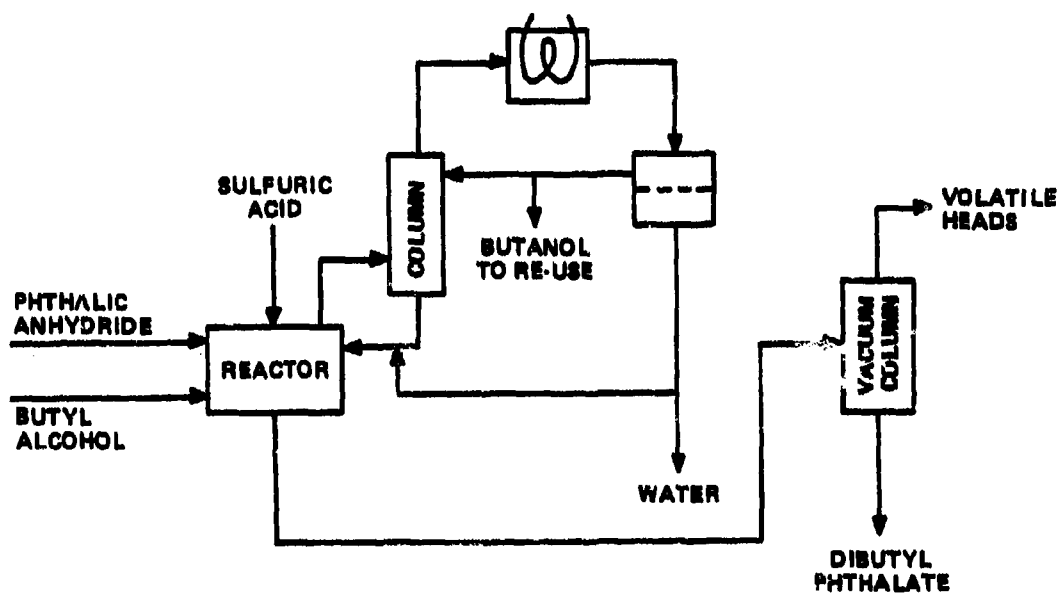


Figure VII-2. Preparation of Dibutyl Phthalate (Lowenheim, 1975).

Table VII-3. Manufacturers of Phthalate Esters (S.R.I., 1977).

Di-n-butyl phthalate

Eastman Kodak Co. Eastman Chem. Products, Inc., subsid. Tennessee Eastman Co.	Kingsport, Tenn.
W. R. Grace & Co. Hatco Group Hatco Chem. Div.	Fords, N. J. Chicago, Ill.
The C. P. Hall Co.	
Internat'l Minerals & Chem. Corp. IMC Chem. Group, Inc., subsid.	Terre Haute, Ind.
Pfizer Inc. Chems. Div.	Greensboro, N. C. Carteret, N. J.
Reichhold Chems., Inc.	
Richardson-Merrell, Inc. J. T. Baker Chem. Co., subsid.	Phillipsburg, N. J.
The Sherwin-Williams Co. Chems. Group Chems. Div.	Chicago, Ill.
Union Carbide Corp. Chem. Products Div.	Dover, Ohio
United States Steel Corp. USS Chems., div.	Neville Island, Pa.

Diethyl phthalate

Eastman Kodak Co. Eastman Chem. Products, Inc., subsid. Tennessee Eastman Co.	Kingsport, Tenn.
Key-Fries Chems. Inc.	Stony Point, N. Y.
Monsanto Co. Monsanto Chem. Intermediates Co.	St. Louis, Mo.
Pfizer Inc. Chems. Div.	Greensboro, N. C.

Di(2-ethylhexyl) phthalate

BASF Wyandotte Corp. Colors and Intermediates Group Colors and Auxiliaries Div. Intermediates Div.	Kearny, N. J. Kearny, N. J.
Eastman Kodak Co. Eastman Chem. Products, Inc., subsid. Tennessee Eastman Co.	Kingsport, Tenn.
The B. F. Goodrich Co. B. F. Goodrich Chem. Co., div.	Avon Lake, Ohio
W. R. Grace & Co. Hatco Group Hatco Chem. Div.	Fords, N. J.
Monsanto Co. Monsanto Indust. Chems. Co.	Texas City, Tex.
Pfizer Inc. Chems. Div.	Greensboro, N. C. Carteret, N. J.
Reichhold Chems., Inc.	
Teknor Apex Co.	Mebromville, Mass.
United States Steel Corp. USS Chems., div.	Neville Island, Pa.

Table VII-4 contains production statistics for the phthalate esters in the U.S. since 1968 and Table VII-5 presents the amount of the individual phthalate esters produced.

Table VII-4. Production<sup>1</sup> and Sales of the Phthalate Esters (U.S. Tarriff Commission).

	<u>68</u>	<u>69</u>	<u>70</u>	<u>71</u>	<u>72</u>	<u>73</u>	<u>74</u>	<u>75</u>	<u>76</u>
Quantity produced	841	884	855	978	1,146	1,203	1,207	904	1,043
Quantity sold	785	821	815	938	1,138	1,135	1,124	921	987

<sup>1</sup>in million pounds

Table VII-5. Production<sup>1</sup> of Selected Phthalate Esters (U.S. Tarriff Commission).

<u>Phthalate ester</u>	<u>72</u>	<u>73</u>	<u>74</u>	<u>75</u>	<u>76</u>
di-ethylhexyl	435.0	378.1	389.7	302.5	296.7
di-butyl	29.1	37.9	35.5	12.3	13.7
di-ethyl	19.0	19.5	19.7	11.7	16.1

<sup>1</sup>in million pounds

Individual plant capacities are unavailable. Due to the similarities of processes, manufacturers who produce more than one ester possess a total phthalate ester production capacity which can be split between different esters depending on current demand.

### 3. Usage

Approximately 95% of all phthalate esters produced in the U.S. are employed as plasticizers. The other 5% is used in a variety of non-plasticized products.

Phthalate esters as plasticizers are found in the construction industry, home furnishings, the automobile industry, synthetic apparel, food packaging, and medical products. The parent alcohols impart varying proper-

ties to the different phthalates making some more suitable than others for individual resin systems.

DEHP, the most widely used phthalate ester, is used exclusively as a plasticizer. Recognized as the best all purposed PVC plasticizer, it is found in most PVC products. It is also used as a plasticizer in nitro-cellulose lacquers, cellulose acetate-butyrate, ethyl cellulose, and natural and synthetic rubbers.

DBP is the standard plasticizer for nitrocellulose and polyvinyl acetate emulsions. It is also used in poly(methyl methacrylate) molding compounds, phenolic resins, and with DEHP and DOP in PVC's. DBP is used as a solvent for printing ink vehicles, insecticides, and oil-soluble vat dyes. It is also used in manufacture of artificial leather, as a fixative for perfumes, and in anti-foam agents (Lowenheim and Moran, 1975).

DEP is almost exclusively used in cellulose acetate plastics. DEP is the preferred plasticizer for non-toxic food packaging film (W. R. Grace Co.).

#### 4. Future Trends

The market for PVC resins is increasing and subsequently future use of phthalate esters should increase accordingly. An average growth rate of 7% has been predicted (Anderson, 1977).

#### 5. Documented or Speculated Occurrences in the Environment

The presence of phthalate esters in the environment has been well documented. They have been identified in the Escambia Bay and the Mississippi River delta (Corcoran, 1973), in the Charles River (Hites, 1973) in the ppb range, in a Lake Superior bay (Stalling *et al.*, 1973), in the North Atlantic and in water, sediment, air and biota samples from the Gulf of Mexico (Giam *et al.*, 1978). Some researchers have questioned the origin of the phthalate esters, suggesting they are either natural products or artifacts of sample handling and analytical techniques. The latter argument is valid and prevention of artifactual contamination of samples is a major difficulty in phthalate ester analysis. But there is little doubt that industrial phthalates are now widespread environmental contaminants (Mathur, 1974).

#### G. Comparison of Civilian and Military Uses of the Phthalate Esters

At 1976 production rates, Radford AAP used 133,360 lb/yr DEP and 434,000 lb/yr DBP. This usage amounted to 0.8% and 3.2% of the DEP and DBP civilian production. At full mobilization, Radford AAP would use ~228,000 lb/yr DEP and 2,496,000 lb/yr of DBP. Radford AAP's use would represent 1.4% and 18.2% of the 1976 civilian production.

No data was available on historical or mobilization usage of DEP and DBP at Badger, Sunflower or Indiana. However, if these AAP's use DEP and DBP

at approximately the same rate as Radford AAP at full mobilization, then the Army could use up to 5.6% of the 1976 U.S. DEP production. The munition use of DBP could be as high as 73% of the 1976 production. Thus, at full mobilization, the Army could become the biggest single user of dibutyl phthalate.

#### H. Toxicological and Environmental Hazards

##### 1. Toxicity to Humans

The toxicology of phthalate esters to man and animals has recently been the subject of several studies. Although the phthalate esters as a group have a low toxicity, the high amounts used by industry warrant this research. Also, small amounts of phthalate esters have been found to leach out of PVC transfusion bags in blood (Jaeger and Rubin, 1970) and other solutions (Guess *et al.*, 1967).

Leaching of DEHP from vinyl plastic transfusion bags has stirred interest in determining levels of DEHP in human tissues. Wallin *et al.* (1974) studied tissue samples from 18 patients. They found DEHP present in all 18 samples. However, they found no correlation between the DEHP concentration and patient's age or receipt of blood transfusion. Napier (1976) studied 43 patients and found only 58% of the tissue samples contained DEHP. He found 27% of the tissues from transfused patients contained DEHP while only 11.6% of the non-transfused patients contained DEHP. The half-life of DEHP in six male patients ranged from 14.6-41.8 minutes, with a mean of 28 minutes (Rubin and Schiffer, 1976).

Some accidental human poisonings by phthalate esters have been reported. For example, an accidental poisoning of a chemical operator with DBP was reported by Cagianut (1954). The man swallowed 10 g (140 mg/kg) of DBP. He became nauseated, dizzy and experienced photophobia, lacrimation and conjunctivitis. However, he quickly recovered from these effects.

##### 2. Mammalian Toxicity

###### a. Acute and Chronic Toxicity

The acute toxicity of the phthalate esters to mammals is presented in Table VII-6. An oral dose of DEP was the most toxic with an LD50 of 1.0 g/kg. These data show that DEP and DBP have a low toxicity. Lawrence *et al.* (1973) injected mice with 5 subacute doses of DEP or DBP per week. As shown in Table VII-7, they observed an apparent LD50 for DEP of  $\sim 1/2$  the acute LD50 after 14 weeks of exposure. For DBP, the apparent LD50 after 25 weeks of exposure was  $\sim 1/4$  the acute LD50.

Smith (1953) fed rats DBP for one year. He found no toxic effects with diets containing 0.25% of DBP. However, half the rats fed 1.25% DBP died during the first week of the experiment. Nikonorow *et al.* (1973) found that 1.2 g/kg/day of DBP increased the mean liver weight of rats. Concentrations of  $2.6 \times 10^{-4}M$  of DEP and  $3.9 \times 10^{-4}M$  of DBP inhibited nerve fiber

Table VII-6. Acute Toxicity of Phthalate Esters: LD50 in Mammals.

Compound	Animal	Route	LD50 g/kg	Reference
Diethylphthalate	Mouse	i.p.	2.8	Patty, 1967
"	Mouse	i.p.	2.8	Calley et al., 1966
"	Mouse	i.p.	3.2	Lawrence et al., 1973
"	Rat	i.p.	5.1	Singh et al., 1972
"	Rat	i.p.	5.06*	"
"	Rabbit	Oral	1.0	Patty, 1967
Dibutylphthalate	Mouse	i.p.	4.0	Calley et al., 1966
"	Mouse	i.p.	3.6	Lawrence et al., 1973
"	Rat	i.p.	3.0	Singh et al., 1972
"	Rat	i.p.	3.05*	"
"	Rat	i.m.	8.0	Smith, 1953
"	Rabbit	Dermal	20.0*	Patty, 1967

\* ml/kg

Table VII-7. Subacute Toxicity of Phthalate Esters in Mice  
(Lawrence *et al.*, 1975)

Week No.	Apparent LD50 (ml/kg) by weeks (intraperitoneal)	
	Diethyl	Di-n-butyl
(Acute LD50)	(2.87)	(3.41)
1	2.26	2.08
2	2.00	1.84
3	2.00	1.84
4	2.00	1.84
5	1.92	1.84
6	1.84	1.84
7	1.77	1.77
8	1.70	1.77
9	1.70	1.70
10	1.70	1.63
11	1.57	1.45
12	1.39	1.39
13	1.39	1.33
14	1.39	1.28
15	--	1.28
16		1.18
17		1.18
18		1.09
19		1.05
20		1.00
21		0.93
22		0.93
23		0.85
24		0.85
25		0.85

growth in rat cerebellum tissue cultures (Kasuya, 1972). Decrease in the activity of succinic dehydrogenase and adenosine triphosphatase were observed in rats injected with DEHP (Srivastava *et al.*, 1975). Reddy *et al.* (1976) found reductions in serum cholesterol and triglyceride levels when DEHP was fed to rats at concentrations of 0.5, 2.0 and 4.0% in food.

#### b. Biochemical Pathways

Williams and Blanchfield (1974) found that almost all of the DEHP ingested by rats was excreted in the urine or feces within 48 hours. Only the adipose tissue consistently retained DEHP. Tanaka *et al.* (1975) observed similar results as Williams and Blanchfield; however, they also observed four metabolites in the urine. Williams and Blanchfield (1975) found 80-90% of an oral dose of DBP to rats is excreted in the urine within 48 hours. They also identified phthalic acid, monobutyl phthalate, mono (3-hydroxybutyl) phthalate, and mono (4-hydroxybutyl) phthalate as metabolites in the urine.

*In vitro* hydrolysis of DEP, DBP and DEHP was highest when exposed to rat small intestine contents (Rowland *et al.*, 1977). DBP was also reduced more rapidly than DEP and DEHP. In addition, these researchers identified the metabolites as the corresponding monoesters.

#### c. Carcinogenic, Teratogenic and Mutagenic Effects

Chronic studies have given no indication of any carcinogenic activity by the phthalate esters (Peakall, 1975). Teratogenic studies by Singh *et al.* (1972) and Nikonorow *et al.* (1973) indicate that DEP, DBP and possibly DEHP are teratogenic at high doses. Their results are presented in Table VII-8. The percentage of resorptions was increased and the fetal weight decreased. An increase in skeletal abnormalities was also observed.

Using the dominant lethal assay in mice, Singh *et al.* (1974) found increased fetal death with single injections of DEHP given at doses of 12.6 to 25.6 ml/kg. At the highest dose, decreased numbers of implants and living fetuses were observed.

### 3. Phthalate Esters in the Aquatic Environment

#### a. Distribution of the Phthalate Esters in the Aquatic Environment

In the past 4 to 5 years, several studies have examined the toxicity of phthalate esters to aquatic organisms. However, information on the levels of the phthalate esters in the aquatic environment is limited. Levels of DBP and DEHP in fish, water and sediment samples taken from industrial and rural areas are shown in Table VII-9. DEHP levels were higher than DBP levels in the samples collected. The most noticeable difference between the two phthalate esters occurred in the water samples where there was approximately 100 times more DEHP than DBP. In addition, the sample from industrialized areas contained more phthalate esters. Williams (1973) reported phthalate ester levels in 21 fish, none exceeding 200 ppb.



Table VII-8. Effects of Diethyl Phthalate and Dibutyl Phthalate on Fetal Development in Rats.

Compound	Dose	Fetus Weight	Number of Resorptions	Reference
Diethyl-phthalate	1.686 ml/kg	2.85*	2 (3.6%)	Singh <i>et al.</i> , 1972
	1.012 "	2.85*	0 (0)	"
	0.506 "	2.63*	28 (44.4%)	"
Dibutyl-phthalate	1.017 ml/kg	3.60*	23 (36.5%)	"
	0.610 "	3.65*	2 (3.6%)	"
	0.305 "	3.70*	4 (7.3%)	"
Dibutyl-phthalate	.120 g/kg/d	3.56	2 (2%)	Nikonorow <i>et al.</i> , 1973
	.600 "	2.92*	22 (28%)	"

\* Significantly different from control ( $P < 0.05$ )

Table VII-9. Levels of Dibutyl Phthalate and Diethylhexyl Phthalate in the Aquatic Environment in ppb  
(Mayer *et al.*, 1972).

<u>Source</u>	<u>Sample Type</u>	<u>DBP</u>	<u>DEHP</u>
Mississippi and Arkansas (agricultural and industrial areas)	Channel catfish	Trace	3,200
Fairport National Fish Hatchery, Iowa	Channel catfish	200	400
(water supply from industrial area of Mississippi)	Dragonfly naiads	200	200
	Tadpoles	500	300
Black Bay, Lake Superior, Ontario (rural and industrial area)	Walleye	—	800
	Water	—	300
	Sediment	100	200
Hammond Bay, Lake Huron, Michigan (forested area)	Water	0.040	—
Lake Huron, Michigan	Water	—	5.0
Spirit Lake, Iowa (agricultural area)	Yellow perch	—	—
Clover Leaf Lake, California (10,300 feet elevation)	Brook trout	—	—
Missouri River, McBaine, Missouri	Water (turbid)	0.09	4.9

b. Acute Toxicity of the Phthalate Esters to Aquatic Organisms

Mayer and Sanders (1973) studied the acute toxicity of DBP to fish and invertebrates as indicated in Table VII-10. They performed standard static and flow-through tests to determine an LC50 (lethal concentration to 50% of the organisms) at 24, 48 and 96 hours. The bluegill was the most sensitive aquatic organism with a 96 hour LC50 of 0.73 ppm, but the overall DBP toxicity was low. Because of its low solubility, the 96 hour LC50 of DEHP was estimated at 10 ppm (Johnson *et al.*, 1976). McKim (1974), in a flow-through test with the scud (*Gammarus fasciatus*), found a 9 week LC50 of 210 ppb for DEHP.

c. Chronic Toxicity of the Phthalate Esters in Aquatic Organisms

Mahrle and Mayer (1976) found that 14 ppb of DEHP significantly increased the mortality of trout fry. DBP levels of 1-5 ppm have been shown to have a depressant effect on the heartbeat of goldfish. However, DEHP had no effect on the heartbeat rate (Pfuderer and Francis, 1975; Pfuderer *et al.*, 1975). Ninety day toxicity studies (Mayer and Sanders, 1973) found DEHP reduced the reproduction of guppies (*Poecilia reticulata*) and zebra fish (*Brachydanio rerio*) receiving levels between 50-100 ppm in their food. Sugawara (1974) found that 10 ppm of DBP and 61 ppm of DEHP significantly reduced the hatching of shrimp eggs. Mayer and Sanders (1973) exposed *Daphnia magna* to 3 and 30 ppm DEHP for 21 days and found reproduction rates were reduced by 60 and 83%, respectively.

d. Bioaccumulation of the Phthalate Esters in Aquatic Organisms

The bioaccumulation of DEHP and DBP from water by aquatic organisms is shown in Table VII-11. High bioconcentration of phthalate esters at levels less than 1 ppb occurred, with the scud having the highest concentration factor. Mayer and Sanders (1973) exposed *Daphnia magna* to 0.1 ppb of labeled phthalate in the water for 7 days. Three days after the *Daphnia* were transferred to fresh water, 50% of the phthalate remained. In 7 days, only 25% of the phthalate remained in the *Daphnia*. Saeger and Tucker (1976) found that phthalate esters in aquatic vertebrates reached a rapid equilibrium with a half-life of approximately 72 hours. Thus, the phthalate esters are quickly removed from the organism.

e. Metabolism of the Phthalate Esters in Aquatic Organisms

Stalling *et al.* (1973) studied the *in vivo* metabolism of DEHP in channel catfish (*Ictalurus punctatus*) and fathead minnows (*Pimephales promelas*). They also conducted *in vitro* metabolic studies with DBP and DEHP by channel catfish enzymes. In both studies, the metabolites were phthalic acid, monoester and/or the glucuronide conjugate. The *in vitro* degradation by the catfish enzymes of DBP was 16 times faster than DEHP. Melancon and Lech (1976) exposed rainbow trout (*Salmo gairdneri*) to 0.5 ppm of radioactive DEHP for 24 hours. They found half of the radioactivity occurred in the bile and that almost all of the radioactivity was due to metabolites of DEHP. After 24 hours, the major metabolite present was mono-2-ethylhexyl phthalate glucuronide.

Table VII-10. Acute Toxicity of Dibutyl Phthalate to Aquatic Organisms

Species	Temperature °C	LC50 ppm			Reference
		24 hr	48 hr	96 hr	
Fathead minnow ( <i>Pimephales promelas</i> )	17	-	1.49	1.30	Mayer & Sanders, 1973
Bluegill ( <i>Lepomis macrochirus</i> )	17	1.23	0.73	0.73	"
Channel catfish ( <i>Ictalurus punctatus</i> )	17	3.72	2.91	2.91	"
Rainbow trout ( <i>Salmo gairdneri</i> )	12	-	-	6.47	"
Scud ( <i>Commurus pseudolimnaeus</i> )	-	7.00	-	2.10	"
Crayfish ( <i>Oreoctes natic</i> )	-	-	-	>10.00	"
Bluegill ( <i>Lepomis macrochirus</i> )	-	-	-	1.18	Hartley, 1977
Ostracod ( <i>Cyclopypris</i> sp.)	-	-	2.53	-	"
Water flea ( <i>Daphnia magna</i> )	-	<5	2.5	-	Warner et al., 1978

Table VII-11. Bioaccumulation of Phthalates from Water by Aquatic Organisms.

Organisms	Phthalate	Water Conc.		Days	Reference
		ppb	Conc. Factor		
Midge larvae ( <i>Chironomus plumosus</i> )	DBP	0.18	6,600	7	Sanders et al., 1973
	DEHP	0.3	3,100	7	"
Waterflea ( <i>Daphnia magna</i> )	DBP	0.08	5,000	7	"
	DEHP	0.3	5,200	7	"
	"	10,000	31	1	Metcalf et al., 1973
	"	"	155	2	"
	"	100	176	1	"
	"	"	182	2	"
Scud ( <i>Grammarus pseudolimnaeus</i> )	DBP	0.10	6,700	14	Sanders et al., 1973
	DEHP	0.1	13,600	7	"
Mayfly ( <i>Hexagenia bilineata</i> )	DBP	0.08	1,900	7	"
	DEHP	0.1	2,300	7	"
Damselfly ( <i>Ishura verticalis</i> )	DBP	0.10	2,700	7	"
Sowbug ( <i>Asellus brevicaudus</i> )	DEHP	1.9	80	7	"
	"	62.3	250	21	"
Catfish ( <i>Ictalurus punctatus</i> )	DEHP	1.0	2,600	1	Stalling et al., 1973
Mosquito larvae ( <i>Culex pipiens</i> )	DEHP	10,000	1,187	1	Metcalf et al., 1973
	"	"	366	2	"
	"	100	318	1	"
	"	"	164	2	"

#### 4. Biological Transformation of Phthalate Esters in the Environment

The phthalate esters can be degraded under aerobic conditions in river water, sediment and activated sludge. In river water, DEHP was partially degraded in 2 weeks; DBP and DEP were completely degraded in 4 to 10 days (Hattori *et al.*, 1975). Saeger and Tucker (1976) found DEHP was biodegradable to 40% of the original concentration in river water 5 weeks and 70% degraded over 24 hours in a semi-continuous activated sludge system. Under aerobic conditions in the sediment, 53% of DBP was degraded within 24 hours and 98% within 5 days; DEHP, however, was only 50% degraded in 14 days (Johnson and Lulves, 1975). Under anaerobic conditions DEHP was not degraded and the degradation rate of DBP was 1/6 of the aerobic degradation rate.

Johnson and Lulves proposed that "Phthalate esters are initially hydrolyzed at the ester linkage to form the phthalate acid half-ester and the corresponding alcohol. We believe this monoester is subsequently degraded, primarily to phthalic acid, by continuous esterase activity in the sediment. We suspect that the exposed carboxyl group of the monoester undergoes decarboxylation to form benzene or salicylate derivatives." Figure VII-3 shows that most likely biodegradation pathway in the presence of oxygen of phthalate esters to straight carbon chain substances (Gibson, 1968).

The release of phthalate esters from Radford AAP (Randall and King, 1971) occurs mainly in the propellant finishing area. Upon release into the aquatic system, the phthalate esters would probably adhere to suspended particles. The use of DBP at Radford AAP is currently 28,000 lb/mo and at full mobilization, approximately 208,000 lb/mo. Since DBP is rapidly degraded in the aquatic environment, its current release into New River poses no long term toxic threat. However, at full mobilization, the system would probably be overloaded and acute stress could occur to the organisms present.

The current usage of DEP at Radford AAP is 19,000 lb/mo and this level would not increase during full mobilization. DEP is rapidly degraded in aquatic systems and poses no long term toxic threat to the organisms present. DEHP is the most persistent of the phthalate esters in aquatic environments, but is not currently used by Radford AAP.

#### 5. Phytotoxicity

Apical chlorosis and 48% growth inhibition were induced in 6-week old *Nicotianum tabacum* by foliar application of a 2500 mg/l solution of dipropyl phthalate. *Elodea canadensis* (pondweed) was found to bioaccumulate DEHP only 3.7 times from water containing 10 mg/l while degrading it very slowly (Metcalf *et al.*, 1973). n-butyl phthalate was reported by Isogai, Komoda and Okamoto (1972) to have a growth-promoting activity in rice seedling bioassays.

No other information has been encountered.

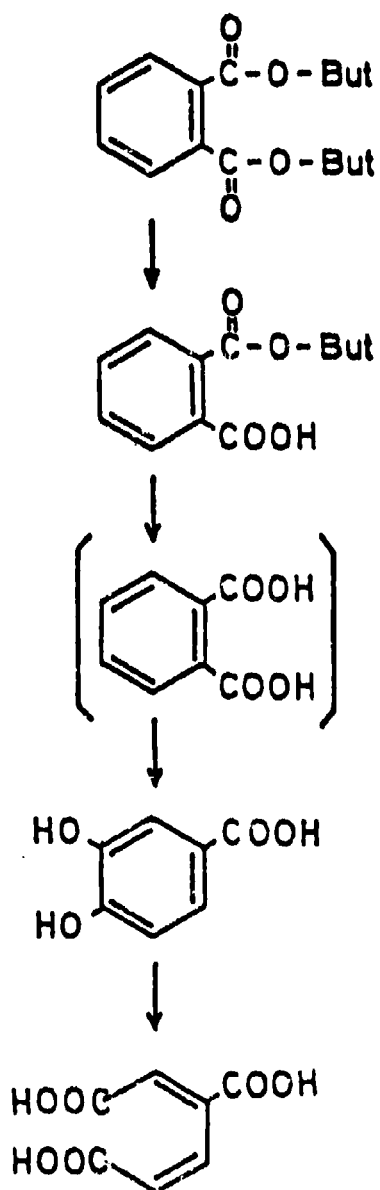


Figure VII-3. Biodegradation Pathway for the Alkyl Phthalates.

## 6. Summary of Environmental and Toxicological Hazards of the Phthalate Ester

The acute toxicity of the phthalate esters is low. Chronic experiment show a high "no-effect" level. However, the phthalate esters have been shown to be teratogenic and mutagenic at high doses. Accumulation factors in aquatic organisms is high. Sufficient information is not available to assess environmental risk associated with these observations.

It appears that mammals can rapidly degrade the phthalate esters. However, the teratogenicity of this compound and the possibility of transformation to a more teratogenic compound (e.g. phthalidamide) needs to be assessed.

## 7. Availability of Literature for Phase II

The phthalate esters have been widely studied. There is sufficient toxicological and environmental literature for a Phase II detailed study.

### I. Regulations and Standards

#### 1. Air and Water Effluent Regulations

A freshwater criterion of 3 mg/l is recommended for the phthalate esters in order to protect aquatic life. Even at this concentration, some reproductive impairment was observed in daphnids (EPA, 1976).

The effluent limitations for manufacture of phthalate esters has been established by EPA. These effluent guidelines are listed in Table VII-12.

Table VII-12. Effluent Guidelines for the Manufacture of Phthalate Esters. (Federal Register, 1976)

Effluent Characteristics	<u>Effluent Limitations</u>	
	Maximum for One Day	Average of Daily Values for 30 Consecutive Days Shall Not Exceed
<u>lb/100 lb of Product</u>		
COD	27	14
BOD 5	0.21	0.011
TSS	0.038	0.021
Total Copper	0.00032	0.00016
pH	Within the range of 6.0 to 9.0	

The phthalate esters are listed in EPA's Toxic Substance Control Act Candidate List of Chemical Substances. These esters are also on the EPA's list of priority pollutants. The environmental effects of the phthalate esters



have been selected as one of the first studies under the Toxic Substances Control Act (Chemical and Engineering News, 1977).

## 2. Human Exposure Standards

Recommended threshold limit values for air exposure to the phthalate esters is 5 mg/m<sup>3</sup> (Federal Register, 1974). This limit is also the suggested values for diethyl and diethylhexyl phthalate. Diethylhexyl phthalate is currently being tested for carcinogenic potency by NCI (1978).

## J. Conclusion and Recommendations

The purpose of this preliminary definition study is to determine the Army's responsibility for conducting further research on the phthalate esters--diethyl-, dibutyl- and diethylhexyl phthalate. Evaluation of the available data on these compounds has lead to the following conclusions:

1. Of the phthalate esters, dibutyl phthalate has the highest use rate by the Army. This chemical is also found at higher levels in the effluent stream. Effluent levels of dibutyl phthalate at full mobilization are estimated to be as high as 4160 lb/month at Radford AAP.
2. Diethyl phthalate is used at a rate of 19,000 lb/month at Radford. This current usage rate is essentially full capacity.
3. Diethylhexyl phthalate is used only occasionally in propellant manufacture.
4. The mammalian toxicity of these esters is low.
5. The phthalate esters are toxic to aquatic organisms in the low ppm range. However, the esters of the lower alcohols are readily biodegradable.
6. At full mobilization, dibutyl phthalate would be toxic to the local ecosystems. The amount of diethyl or diethylhexyl phthalate discharged from propellant manufacture is not high enough to cause an environmental problem.

After evaluation of the information gathered during this study, it is concluded that further research on diethyl and diethylhexyl phthalates should be a low priority. Further Army-sponsored studies on dibutyl phthalate are of questionable value. Sufficient information exists on the mammalian toxicity of these chemicals. However, further study on the environmental properties of dibutyl phthalate may be warranted. If further work on dibutyl phthalate is undertaken, it is recommended that a thorough literature search and evaluation on the environmental fate of this compound be conducted.

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AD

PRELIMINARY PROBLEM DEFINITION STUDY OF  
48 MUNITIONS-RELATED CHEMICALS

VOLUME II PROPELLANT RELATED CHEMICALS

TRIACETIN

FINAL REPORT

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PRELIMINARY PROBLEM DEFINITION STUDY OF  
48 MUNITIONS-RELATED CHEMICALS

VOLUME II PROPELLANT RELATED CHEMICALS

TRIACETIN

FINAL REPORT

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COTR: Clarence Wade, Ph.D.

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## SUMMARY

Triacetin is used as a plasticizer in solid propellant formulations. These formulations contain 3.25 to 11.0% triacetin. At the present time only Radford AAP uses triacetin. Current use rate is ~ 43,000 lb/year. At full mobilization 150,000 lb/year would be used by Radford. Sunflower and Badger would use similar amounts at full mobilization.

. Estimated losses of triacetin from current propellant manufacture are between 180 and 540 lb/month. At full mobilization up to 2000 lb/month could be lost at each plant using triacetin. Since this compound is readily soluble in water, virtually all the triacetin lost will be in the waste streams.

Triacetin is produced in the United States by three manufacturers. Current production capacities are estimated at 1 million lb/year. Triacetin has a wide variety of uses in the civilian community including a plasticizer in cigarette filters, a solvent and carrier in pharmaceutical preparations, a solvent and fixative in perfumes and flavors, etc. Because of the widespread use of triacetin in disposable items, the civilian pollution of triacetin is also expected to be widespread.

Mammals exhibit a low toxic response to triacetin. However, aquatic organisms and invertebrates are fairly sensitive to this chemical. At full mobilization, significant effects on the local aquatic population near Radford, Sunflower and Badger could occur. Microorganisms should readily degrade this compound, precluding any widespread damage to the ecosystem.

At current production levels, the Army uses only 4% of the triacetin civilian production capacity. At full mobilization, the Army usage of this chemical could be as high as 45% of the civilian capacity. Although the Army use rate of triacetin could be high under emergency conditions, this chemical is not a military unique compound.

The only Army problem with triacetin appears to be potential local aquatic effects. The planned biotreatment facility at Radford should adequately remove this compound from Radford's waste streams. From these findings it appears that triacetin has a low priority for inclusion in the Phase II work. If it were to be included, the study should be limited to environmental toxicology and fate.

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## FOREWORD

This report details the results of a preliminary problem definition study on triacetin. The purpose of this study was to determine the Army's responsibility for conducting further research on triacetin in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on triacetin, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Triacetin was only one of the 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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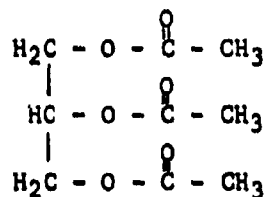
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## VIII. TRIACETIN

### A. Alternate Names

Triacetin is the triacetate ester of glycerine. It has a molecular formula of  $C_9H_{14}O_6$  and a molecular weight of 218.21 g/mole. The structure of triacetin is shown below:



The pertinent alternate names for triacetin are as follows:

CAS Registry No.:	102-76-1
CA Name (9 CI):	1,2,3-propanetriol, triacetate
CA Name (8 CI):	Acetin, tri-
Wiswesser Line Notation:	1V01YOV181OV1
Synonyms:	Enzactin; Fungacetin; Glycerin triacetate; Glycerol triacetate; Glyceryl triacetate; Glyped; Kasscoflex TRA; Triacetin; Triacetine; Vanay

### B. Physical Properties

The physical properties of triacetin are presented in Table VIII-1. The infrared spectrum of the compound is shown in Figure VIII-1.

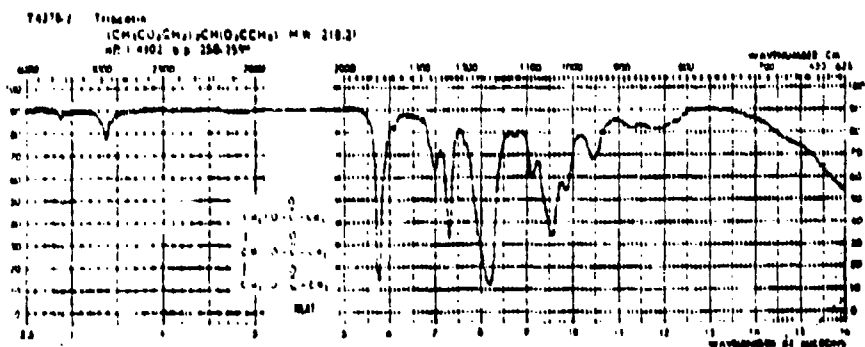


Figure VIII-1. Infrared Spectrum of Triacetin (Pouchert, 1970).

Table VIII-1. Physical Properties of Triacetin.\*

Physical Form @ 20°C:	oily liquid
Color:	colorless
Odor:	fatty
Taste:	bitter
M.P.:	-78°C 5.2 (supercools to ~ -70°C) (Eastman Chemical)
B.P.:	258°C @ 760 mmHg 172°C @ 40 mmHg
Vapor Pressure:	0.0025 mmHg @ 50°C
Liquid Density:	$d_4^{25}$ 1.1562; $d_4^{20}$ 1.1596; $d_{20}^{20}$ 1.163
Vapor Density (air=1):	3.17
Refractive Index:	$n_D^{20}$ 1.4296; $n_D^{25}$ 1.4307
Flash Point:	153°C open cup
Autoignition Temperature:	432°C
Lower Explosive Limit in Air (189°C):	1.05% vol
Solubility:	water - 6.12g/100g @ 20°C soluble in alcohol, ether, chloroform and other organic solvents

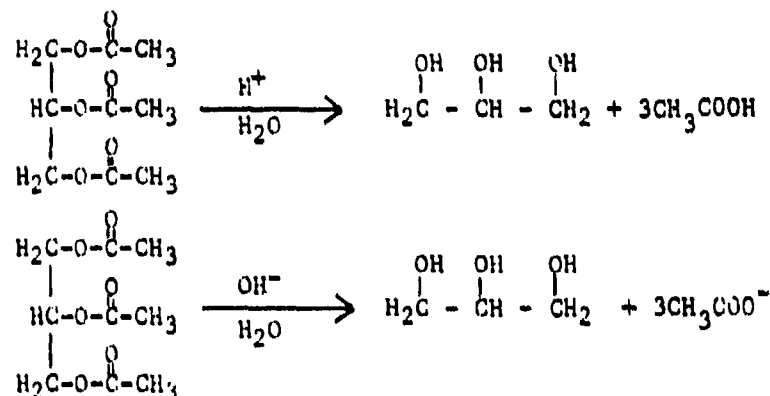
\*References: Eastman Chemical, 1976; Windholz, 1976; Hawley, 1977.

## C. Chemical Properties

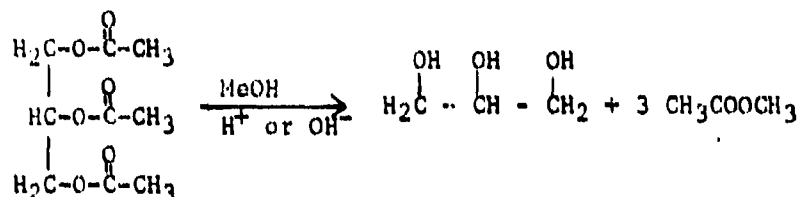
### 1. General Reactions

Triacylglycerols of various long chain carboxylic acids occur naturally as the major components of neutral storage fats in plants and animals. Triacetin is the common name for triacetyl glycerol, the acetate analog of the neutral fats.

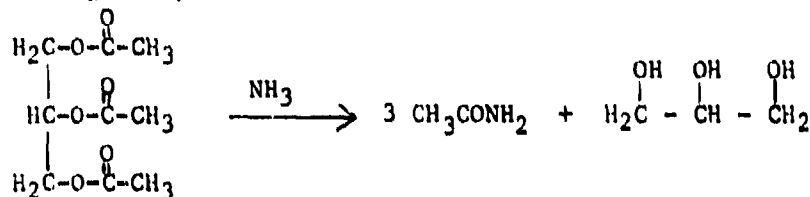
Hydrolysis to glycerol and acetic acid occurs readily. A boiling aqueous solution of triacetin is 91% hydrolyzed after 96 hours (Eastman Chemical, 1976). Either acid or base speeds the hydrolysis. In base, the carboxylate salt of acetic acid is formed.

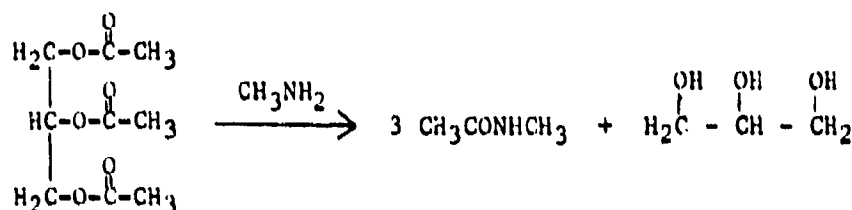


In alcohol solutions, triacetin undergoes transesterification reactions. In methanol, the reaction gives glycerol and methyl acetate.

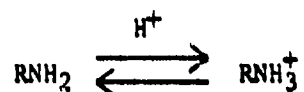


Nitrogen nucleophiles such as ammonia or alkylamines will attack the ester linkage to produce amides.

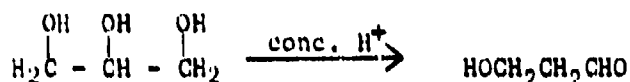




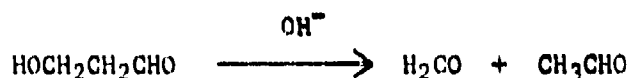
Amide formation occurs more readily than hydrolysis or alcoholysis and is essentially irreversible. It will not occur in acidic solutions where the nitrogen compounds exist as non-nucleophilic ammonium ions.



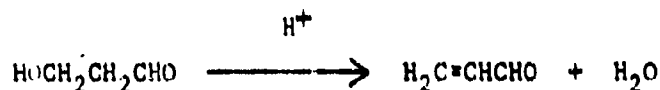
Treatment of triacetin with strong acid could result in several reactions following hydrolysis. Either dehydration or a pinacol type rearrangement of glycerol would form 3-hydroxy propionaldehyde.



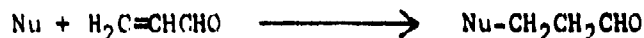
The hydroxyaldehyde can either decompose to acetaldehyde and formaldehyde in a reverse Aldol condensation



or eliminate a second molecule of water to form 2-propenal.

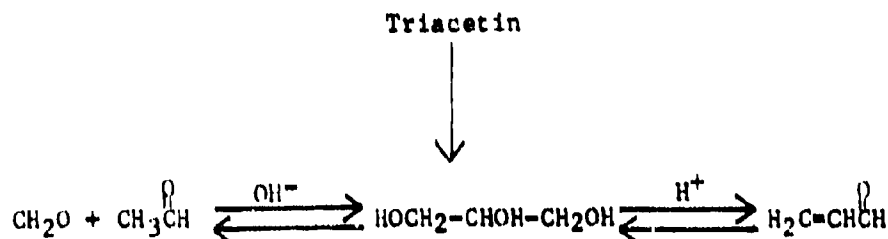


The  $\alpha$ - $\beta$  unsaturated aldehyde can act as a Michael acceptor, undergoing nucleophilic addition at the  $\beta$  position



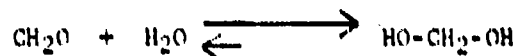
## 2. Environmental Reactions

Triacetin will hydrolyze slowly in neutral waters. Hydrolysis occurs more rapidly in acidic or alkaline environments.





If the acidity is high enough to promote formation of 6-hydroxypropionaldehyde, the above equilibrium will be established. Dissipation of formaldehyde and acetaldehyde and the favored formation of the gem-diol in water will prevent recondensation, resulting in net chemical degradation of triacetin to the lower aldehydes and acetic acid.



### 3. Sampling and Analysis

Sopranetti and Reich (1977) used a Perkin-Elmer 900 gas chromatograph with a flame ionization detector to determine triacetin along with nitroglycerin, dinitrotolulene, diphenylamine, and dibutylphthalate.

A gas chromatographic procedure has been developed for analysis of triacetin in a mixture of acetins, allyl acetate and acetic acid (Tragaevet *et al.*, 1976).

Trowell (1969, 1970) determined triacetin by gas chromatography in aged double base propellants. Quantitative analysis of triacetin was performed along with 2-nitrodiphenylamine, dimethyl sebacate, dimethyl phthalate, resorcinol, and mono-, di-, and trinitroglycerine.

Landram *et al.* (1970) used dry-column chromatography to separate triacetin from other components in double base propellants. Quantitative determination was done by IR absorbance at  $1745\text{ cm}^{-1}$ .

### D. Uses in Army Munitions

#### 1. Purposes

Triacetin is used as a plasticizer in the following propellant formulations:

	<u>% Triacetin in formulation</u>
NOSIH-AA-6	3.25
RAP	8.8
PNJ	8.16
Bermite	11.0

These formulations are double base propellants made by both solvent and solventless processes. Triacetin is currently in use only at Radford AAP, although it has been used in the past at Badger AAP and Sunflower AAP as well.

## 2. Quantities Used

### a. Historical Use

During the period 1968-1977, Radford AAP processed an average of 68,700 lb/year of triacetin. About 1/3 of this amount was used for solventless propellants. An additional 1/6 was used for solvent process double base formulations. The remainder was not accounted for by propellant production statistics.

The specific amount of triacetin purchased by RAAP during 1968-1977 is given below (Watts, 1978):

<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
80,000	80,000	0	0	39,830	198,560	160,690	41,980	43,280	43,040

### b. Current Use

The average use rate of triacetin at Radford AAP was about 5,900 lb/month during 1977. None of the formulations specifying triacetin were produced during December 1977, so the rate of consumption for that month was zero.

### c. Use at Full Mobilization

At full mobilization, 12,200 lb/month of triacetin would be used at Radford AAP. The average use rate during 1977 represented about 48% of the full mobilization use rate.

## 3. Documented or Speculated Occurrences in Air or Water

The specific concentration of triacetin in propellant waste effluents has not been measured. Effluents containing triacetin would be derived from the following sources:

- Preparation operations including weighing, grinding or classification. Dust or particulates are collected in wet scrubbers, from which both solid wastes and contaminated effluents may be generated.
- Residues from washdown operations generate effluents which are filtered and discharged. Collected solids are transported to the burning grounds.
- Process water from manufacture of propellants by the solvent process. These effluents appear in the C-line waste water stream, the 48 inch general purpose sewer at the solvent recovery area discharges.

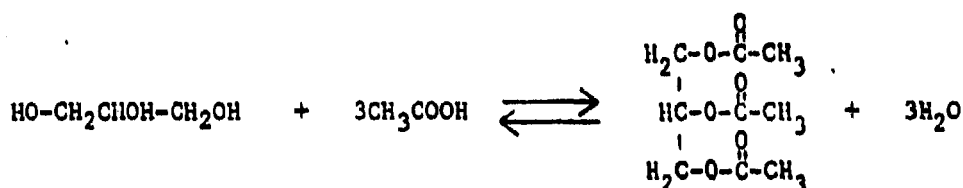
- Process wastes from solventless propellant manufacture. These effluents appear in the rolled powder area waste streams.

Approximately 1-6% of the double base propellants produced are lost to waste streams (Dickenson, 1978). This would account for an average loss of 60 to 360 lb/month of triacetin based upon 1977 use rates. Additional losses from chemical preparation operations would be approximately 120 to 180 lb/month. Thus, total current losses of triacetin are on the order of 180 to 540 lb/month. At full mobilization, these losses would rise to 700 to 2000 lb/month. Due to the high solubility of triacetin in water, virtually all the triacetin lost will be present in the waste streams.

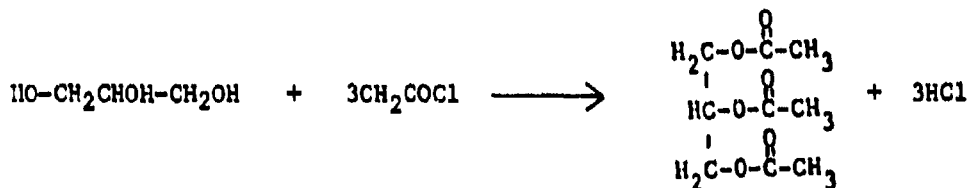
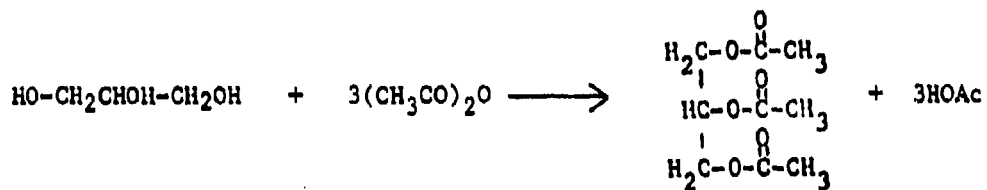
#### E. Uses in the Civilian Community

##### 1. Production Methodology

Triacetin is prepared by direct acetylation of glycerol. This reaction may be accomplished with either acetic acid, acetic anhydride or acetyl chloride. Acetylation with acetic acid is an equilibrium process which is driven by removal of water from the system.



Acetylation with acetic anhydride or acetyl chloride is irreversible.



Triacetin may also be produced by treatment of a liquid mixture of allyl acetate and acetic acid with  $O_2$  in the presence of a bromine catalyst.

## 2. Manufacturers, Production, and Capacities

The three U.S. manufacturers of triacetin are listed below (S.R.I. 1977).

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Table VIII-2. U.S. Manufacturers of Triacetin.

		<u>Use</u>
Armak Indust. Chem. Div.	Phil., PA	primarily captive
Union Carbide, Chem. & Plastics Div.	Institute, W.VA., South Charleston, W. VA.	primarily sales
Eastman Chemical Products Inc.	Kingsport, TN	primarily sales

---

Armak is currently operating at a capacity of 30,000 pounds per month. Union Carbide and Eastman's capacities are unavailable. Historical production figures are also unavailable.

## 3. Usages

Triacetin's primary use is as a plasticizer in cellulose resins. Minor uses include: a solvent and carrier in pharmaceutical preparations, a solvent and fixative in perfumes and flavors, and an ingredient in inks for printing on nonabsorbent surfaces (Eastman Chemicals, 1976).

## 4. Future Trends

No new uses for triacetin are anticipated.

## 5. Documented or Speculated Occurrences in the Environment

Triacetin occurs naturally in the seed of *Euonymus europaeus* (Kirk and Othmer, 1966). It has been observed in ethanol extracts from cigarette filters (Constantinescu, 1974). Because of its widespread use in disposable items, significant quantities of triacetin are expected to be found in the environment from civilian usages.

## F. Comparison of Civilian and Military Uses of Triacetin

Triacetin is produced by three manufacturers in the United States. Although total capacities and production statistics are unavailable, a good estimate of current capacity is 1 million lb/year. At current production rates, Radford AAP uses 43,000 lb/year or about 4% of the United States production capacity. At full mobilization, Radford AAP use of triacetin would be 150,000 lb/year. If Badger and Sunflower also use this chemical at a full mobilization rate of 150,000 lb/year, the total Army usage would be 45% of the civilian production capacity. Although triacetin is not a military unique chemical, at full mobilization of all propellant plants, the military uses of triacetin could account for almost half of the United States production capacity.

## G. Toxicological and Environmental Hazards

### 1. Toxicity to Mammals

Triacetin has a low toxicity to mammals. The oral and intraperitoneal LD50 for rats and rabbits is presented in Table VIII-3. Triacetin is most toxic (LD50 = 1.8 - 1.6 g/Kg) when intraperitoneal doses are given. Shapira et al. (1976) substituted triacetin for fat in rat diets. They found that 30-40% of triacetin in the total diet still produced normal weight gains. Patty (1963) also reported triacetin in rat diets produced normal weight gains in levels up to 55%.

### 2. Aquatic Toxicity

The distribution of triacetin in the aquatic environment has not been studied. Warner et al. (1978) found a 48 hour EC50 (effective concentration to 50%) for *Daphnia magna* to be between 1-5 ppm. Using the fathead minnow (*Pimephales promelas*), the 96 hour LC50 was 223 ppm. From this data triacetin is moderately toxic to aquatic organisms.

Radford AAP's current uses of triacetin range from 5900 lb/mo to 12,200 lb/mo at full mobilization. Loss estimates are 180-540 lb/mo at current production rates and 700-2000 lb/mo at full mobilization. Since triacetin is very soluble in water (61 g/l), virtually all the triacetin lost will be found in the waste streams. Table VIII-4 shows the levels of triacetin that could be found at different flow rates and degrees of mixing. From this data and the acute toxicity studies, triacetin could have some toxic effects on aquatic organisms in a limited area of New River. However, at a low pH, triacetin will be hydrolyzed to acetic acid and glycerol.

Table VIII-3. Toxicity of Triacetin to Mammals.

<u>Species</u>	<u>Dose (g/kg)</u>	<u>Route of Adminis.</u>	<u>Effects</u>	<u>Reference</u>
Rats	6.4-12.8	Oral	LD50	Eastman Chem. Co., (1976)
Mice	3.2-6.4	Oral	"	"
Rats	0.8-1.6	Intraperitoneal	"	"
Mice	0.8-1.6	Intraperitoneal	"	"
Mice	8.0	Oral	"	Lawrence et al., (1974)
Mice	1.52	Intraperitoneal	"	"

Table VIII-4. Triacetin Levels (ppm) in New River at Full Mobilization.

<u>Degree of Mixing</u>	<u>Low Flow (336 mgd)</u>	<u>Average Flow (2500 mgd)</u>
1%	2.4	0.31
10%	0.24	0.03
100%	0.02	0.003

### 3. Toxicity to Microorganisms

Triacetin, because of its water solubility (61 g/l water), is used as a carrier in fungicidal compositions (Kirk and Othmer, 1966). It is doubtful that it is toxic to the microorganisms. At a low pH, triacetin will slowly hydrolyze to acetic acid and glycerol and both of these compounds would be easily metabolized by microorganisms.

### 4. Availability of Literature for Phase II

Although the amount of toxicological and environmental literature on triacetin is not plentiful, sufficient literature appears to be available

for a Phase II study. Literature is also available on toxicological and environmental properties of similar glycerol derivatives.

#### H. Regulations and Standards

There are no standards or regulations directly applicable to triacetin. However, this compound is listed in EPA's "Toxic Substances Control Act List of Candidate Chemical Substances".

#### I. Conclusions and Recommendations

The goal of this preliminary problem definition study was to determine the Army's responsibility for conducting further research on triacetin. From the data evaluated during this study and presented in this report, the following conclusions can be drawn.

1. Triacetin is not a military unique compound. However 45% of the civilian production capacity could be used in propellant manufacture under full mobilization conditions.
2. The civilian uses of triacetin are wide spread; the civilian pollution is also widespread.
3. Mammals exhibit a low toxic response to triacetin.
4. Aquatic and invertebrate life are fairly sensitive to this compound with reported LC50's in the range of 1-250 ppm.
5. At full mobilization, significant effects on aquatic life near Radford, Badger and Sunflower could occur.

Further environmental studies on triacetin could be of some benefit. However, triacetin should be effectively eliminated from the waste streams at Radford AAP when the new treatment facility is in operation. Therefore, any further environmental studies on this compound should be low priority.

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U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND  
Fort Detrick, Frederick, Maryland 21701

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## SUMMARY

Lead salicylate is used as a burning rate modifier in solvent and solventless double base propellants. This compound is currently only used at Radford Army Ammunition Plant. At current production rates, 3000 lb of lead salicylate are used at Radford AAP each month. This usage represents full production capacity of the propellants employing lead salicylate in their formulations. Losses of lead salicylate to the environment from Radford AAP operations are estimated at 45-150 lb/month.

Lead salicylate is manufactured by one civilian firm. Potential production capacities for this chemical are estimated at ~ 1 million lb/year. In the civilian market, lead salicylate is used as a stabilizer in flooring and other vinyl compounds requiring good light stability.

Lead salicylate is toxic to mammals. It is readily absorbed through the skin. The aquatic toxicity of this compound is unknown. However due to the limited solubility of lead salicylate, the aquatic toxicity is probably low.

The absence of production statistics makes an evaluation of the military versus civilian usage difficult. However, it is estimated that the Army uses ~ 1/3 - 1/2 of the lead salicylate produced by the civilian community. The Army propellant manufacture is probably the main source of environmental pollution of this compound. Therefore, it is recommended that lead salicylate be included in the detailed Phase II toxicological and environmental evaluations.

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## FOREWORD

This report details the results of a preliminary problem definition study on lead salicylate. The purpose of this study was to determine the Army's responsibility for conducting further research on lead salicylate in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on lead salicylate, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Lead salicylate was only one of the 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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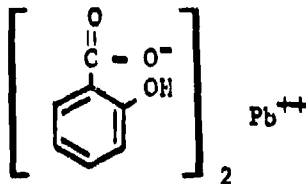
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## IX. LEAD SALICYLATE

### A. Alternate Names

Lead salicylate is a stabilizer used in vinyl compounds requiring good light stability. Lead salicylate has a molecular formula of  $C_{14}H_{10}O_6Pb$  corresponding to a molecular weight of 481.21 g/mole. It has the following structure



Pertinent alternate names for lead salicylate are listed below:

CAS Registry No.:	15748-73-9
Alternate Registry No(s).:	16183-13-4; 14901-86-5; 824-37-3
CA Name (9CI):	Lead, bis(2-hydroxybenzoato-O(1), O(2))-,(T-4)-
CA Name (8CI):	Lead, bis (salicylato)-
Synonyms:	Salicylic acid, lead(2+)salt(2:1); Benzoic acid, 2-hydroxy-, lead(2+) salt(2:1)

### B. Physical Properties

The physical properties of lead salicylate are presented in Table IX-1.

Table IX-1. Physical Properties of Lead Salicylate (Hawley, 1977).

Physical Form @ 20°C:	soft crystalline powder
Color:	creamy white
M.P.:	N.A.
B.P.:	N.A.
Specific Gravity:	2.3 g/cm <sup>3</sup>
Refractive Index:	1.78
Solubility:	soluble in hot water and alcohol

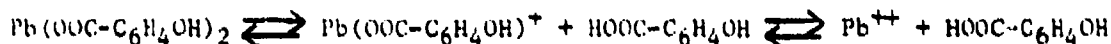
### C. Chemical Properties

#### 1. General Reactions

Detailed investigations into the chemical behavior of lead salicylate have not been reported in the literature. Lead salicylate is soluble in hot water and has some solubility in cold water. Step-wise hydrolysis



will probably occur upon dissolution.



This hydrolysis and thus the solubility of lead salicylate should increase as the pH decreases. In solutions of high pH, lead salicylate would be expected to form soluble basic salts. These reactions will occur in the environment depending on the conditions encountered.

## 2. Sampling and Analysis

Quantitative analysis of organolead compounds may be accomplished by removing the organic constituent by oxidation. The resulting lead oxide may be determined by atomic absorption. Lead may also be determined colorimetrically with dithizone. The red lead dithizonate is quantitated by absorption at 520 nm (Franson, 1975).

## D Uses in Army Munitions

### 1. Purposes

Lead salicylate is used in the production of both solvent and solventless double base propellant. The following formulations require lead salicylate:

#### % Lead Salicylate in Formulation

RAP	1.2
RAP/8	1.2
PNJ for TOW	1.93
PNJ casting powder	2.93
ARP casting powder	3.0 ± 2.5
AHH casting powder	2.3
N-S	1.2
NOSIH-AA-2	1.5
NOSIH-AA-6	1.5
Bermite	2.5

Currently, lead salicylate is used only at Radford AAP. In the past, it has been used at Badger AAP and Sunflower AAP.

### 2. Quantities Used

#### a. Historical Use

During 1968-1977, Radford AAP purchased an average of 46,000 lb/year of lead salicylate. Propellant production accounted for about 53% of this amount, with 78% of the lead salicylate used in propellants going

into solventless formulations, predominantly N-5 and NOSIH-AA-6. The remaining 47% of the purchased amounts were sent to other propellant facilities, or in some cases, returned to the vendor.

The specific amounts of this lead compound purchased by Radford AAP during 1968-1977 are listed below (Watts, 1978):

<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
206,800	83,600	0	0	0	28,000	66,000	10,200	24,200	39,600

b. Current Use

During 1977, Radford AAP used lead salicylate at the rate of about 3000 lb/month. In December, 1977, the use rate was at this level for production of 100,000 lb of ARP casting powder by the solvent process.

c. Use at Full Mobilization

The current use rate of lead salicylate, 3000 lb/month, also represents the full mobilization use rate of this material.

3. Documented or Speculated Occurrences in Air or Water

The actual concentration of lead salicylate in waste streams at Radford AAP has not been measured. Effluents containing lead salicylate would be expected to be generated from the following sources:

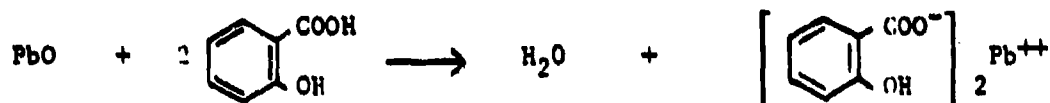
- (1) Preparation operations including weighing, grinding or classification. Dust or particulates are collected in wet scrubbers, from which both solid wastes and contaminated effluents may be generated.
- (2) Residues from washdown operations generate effluents which are filtered and discharged. Collected solids are transported to the burning grounds.
- (3) Process water from manufacture of propellants by the solvent process. These effluents appear in the C-line wastewater stream, the 48-inch general purpose sewer and the solvent recovery area discharges.
- (4) Process wastes from solventless propellant manufacture. These effluents appear in the rolled powder area waste streams.

It is estimated that 1-6% of the double base propellants produced are lost during solvent processing operations. Solventless propellant processing normally results in losses of 1-5% (Dickinson, 1978). Another 2-4% of the lead salicylate used may be lost during preparation operations. Thus, the total losses of lead salicylate to waste streams is estimated at 90-300 lb/month. This figure is also representative of full mobilization operations. It is estimated that 1/2 of the lead salicylate lost eventually enters the New River.

## E. Uses in the Civilian Community

### 1. Production Methodology

Lead salicylate is produced by the reaction of litharge (yellow lead oxide) and salicylic acid (NL Industrial Chemicals, 1978).



The precipitate is filtered and the reaction medium recycled to reclaim dissolved materials. The lead salicylate is washed, then dried under dust collection. Figure IX-1 is a flow diagram of the process.

### 2. Manufacturers, Production and Capacities

Lead salicylate is manufactured under the trade name Normasal by NL Industries at plants in Oakland, California and Philadelphia, Pennsylvania. Production figures, plant capacities and details of the production process are unavailable due to their proprietary nature.

### 3. Usages

Lead salicylate is used as a stabilizer in flooring and other vinyl compounds requiring good light stability (Hawley, 1977).

### 4. Future Trends

No new civilian applications for lead salicylate are anticipated.

### 5. Documented or Speculated Occurrences in the Environment

No environmental occurrences of lead salicylate have been reported.

## F. Comparison of Military and Civilian Uses and Pollution

The civilian usage of lead salicylate is not as wide spread as the other lead soaps such as the stearate. Civilian production is less than 1 million pounds per year. Due to the similarity in production processes for many of the metallic soaps, facilities could be converted to lead salicylate manufacture to meet market demands. For this reason, actual civilian production capacity could be much greater than 1 million pounds per year.

Current use rate of lead salicylate at RAAP is ~3000 lb/month. This number also represents projected mobilization usage. If Sunflower and Badger were using lead salicylate at the same full mobilization rate, the Army would be using 108,000 lb/yr. This number appears to be a low estimate since RAAP alone purchased over 200,000 lb of lead salicylate in 1968.

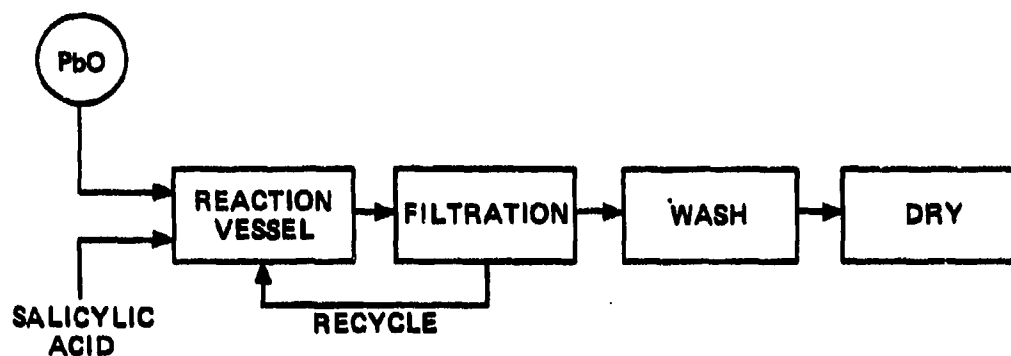


Figure IX-1. Manufacture of Lead Salicylate.

At current use rate, the Army is probably one of the major users of lead salicylate. The Army's current purchases are estimated to be 20% of the civilian production of this chemical. At full mobilization, with all propellant plants operating, the Army usage would be 40% of the civilian production.

The Army is probably one of the major polluters of lead salicylate. However, when compared to total U.S. lead pollution, any lead salicylate entering the environment for propellant production is small. However, the potential danger to the local aquatic system around the propellant manufacturing plants is not small.

#### G. Toxicological and Environmental Hazards

##### 1. Toxicity to Mammals

No mammalian toxicological studies specifically on lead salicylate were uncovered in the recent literature. However, Sax (1976) indicates that lead salicylate is toxic and readily absorbed through the skin.

##### 2. Aquatic Toxicity

Aquatic toxicity studies on lead salicylate are nonexistent, however, the toxicity of other low soluble organic-lead compounds is low (Cairns and Dickson, 1971). The stability of lead salicylate in aquatic systems has not been studied. However, it is likely that a substantial amount of lead salicylate is degraded to  $Pb^{++}$  either through chemical processes or by microorganisms. The lead will be precipitated as the hydroxide, carbonate or sulfate depending on the environmental conditions encountered.

The aquatic toxicity of lead to the aquatic environment is well documented (Lambou and Lim, 1970). Bioassay data available indicate that lead is more toxic in soft water (less than 50 ppm  $CaCO_3$ ) than in hard water systems. This difference in toxicity is due to the unavailability of ionic lead in hard water systems.

Losses of lead salicylate from Radford AAP operations to the New River are estimated at 45-150 lb/month. Lead salicylate has a low solubility in cold water and most of the compound will be found in the sediment. A study by Weitzel et al. (1976) appears to confirm this conclusion. They found total lead levels in New River water to be between 1-2 ppb. Lead levels in the sediment averaged greater than 100 ppm.

The acute effects of lead salicylate on the aquatic organisms in New River are probably minimal. However, the long term accumulation of lead compounds in the sediment would gradually increase the toxicity of the sediment in New River near Radford AAP and further downriver where sediment particles would accumulate.

### 3. Toxicity to Microorganisms and Invertebrates

No data on the toxicity of lead salicylate to microorganisms or invertebrates was found in the literature.

### 4. Phytotoxicity

No phytotoxic information on lead salicylate was encountered. However, phytotoxic data on lead was obtained and may be indirectly related.

The pattern of lead uptake by plants has been rarely studied and little can be concluded about the mechanism involved. The uptake of lead was reported constant with increasing levels of soil lead, until a certain point is reached when uptake becomes unrestricted and rises abruptly (Nicolls *et al.*, 1965).

Only soluble lead salts and ionic lead are available to plant roots. The uptake of lead by ryegrass grown in a solution containing lead is shown in Table IX-2 (Hepple, 1972). The total content of lead in roots plus shoots of perennial ryegrass increases with increasing levels in the soil. The roots take up lead readily but pass on only a small proportion to the shoots. Thus, the roots act as a barrier which restricts the movement of lead salt through the plant to growing animals. During winter months when plant growth is low, a considerable increase in the lead contents of the ryegrass shoots was observed. An 8-fold increase in total lead content of a soil did not cause any significant increase in the lead content of bromegrass grown on the soil in a greenhouse (Motto *et al.*, 1970).

Corn was grown in the field where lead acetate had been soil-applied at eight rates ranging from 0 to 3,200 kg lead/ha. No change in emergence, plant height, grain yield, color, maturity or other growth differences were observed during the 2-year study (Baumhardt and Welch, 1972).

Five crops (cauliflower, tomatoes, cabbage, strawberries and valencia oranges) were analyzed for their lead content by Schuck and Locke (1970). These plants revealed little inclinations to absorb lead via their root system (Schuck and Locke, 1970).

### 5. Availability of Literature for Phase II

There is very little recent U.S. literature on lead salicylate. Toxicological and environmental information would have to come from the foreign literature and the manufacturers files.

Table IX-2. Lead Uptake by Perennial Ryegrass Grown  
in Solution-Culture (Hepple, 1972).

Level of Pb added to solution		Pb content of plants at 14 days after addition to solution			
		Roots		Shoots	
(ppm)	( $\mu$ g)	(ppm)	( $\mu$ g)	(ppm)	( $\mu$ g)
0.4*	400	98	201	3	37
1.0†	12500	3696	9610	104	1055

\* In 1 liter of static solution-culture; controlled environment.  
experiment.

† In 12.5 liter of flowing solution-culture; glass-house experiment.

## H. Regulations and Standards

### 1. Air and Water Standards

There are no air and water standards specific for lead salicylate. However, criteria have been set for lead in potable and effluents (EPA, 1976). For potable water the lead content can be no greater than 50 µg/l. Due to the variability of lead solubility and toxicity in different waters, the following criterion has been set for effluents (using the receiving water as a diluent).

- 0.01 times the 96-hour LC50 value expressed as dissolved lead for the most sensitive species.

This criterion requires that 96-hour LC50 test be performed with the actual water samples and the most sensitive species in the local ecosystem.

### 2. Human Exposure Standards

No specific standards for lead salicylate have been set for occupational exposure to this chemical. However, a criteria document has recommended an air standard of 150 µg(Pb)/m<sup>3</sup> for lead stearate (NIOSH, 1977). A similar TLV for lead salicylate should afford workers adequate protection.

## I. Conclusions and Recommendations

During the preliminary problem definition study, we have attempted to evaluate the military and civilian usage and pollution of lead salicylate. Due to the proprietary nature of the civilian production of this chemical, only estimates can be made of the percentage of the civilian production of lead salicylate used by the Army. It is estimated that the Army uses 1/3 to 1/2 of the amount of this compound produced in the United States each year. The Army's propellant production is also probably the main source of pollution of this chemical.

Lead salicylate is toxic to mammals, being absorbed through the skin. Its toxicity to aquatic organisms is probably low. Accumulation of the lead salicylate and lead resulting from breakdown of this compound is expected to occur in the sediment of the New River.

Based on the information uncovered in this study, the following studies are recommended

- Phase II detailed analysis of the toxicological and environmental literature
- analysis of sediment samples and biota to determine accumulation of lead salicylate
- aquatic toxicity studies may be warranted depending on the results of the Phase II study.



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AD

PRELIMINARY PROBLEM DEFINITION STUDY OF  
48 MUNITIONS-RELATED CHEMICALS

VOLUME II PROPELLANT RELATED CHEMICALS

LEAD STEARATE

FINAL REPORT

J. F. Kitchens  
W. E. Harward III  
D. M. Lauter  
R. S. Wentzel  
R. S. Valentine

April 1978

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#### SUMMARY

Lead stearate is used in the berrite grains and the ROLAND propellant as a burning rate modifier. These propellants are not currently being produced by the Army. If these propellants were produced at full capacity, 500 lb/month of lead stearate would be used at Radford AAP.

The civilian production of lead stearate was 1,254,000 lb/year in 1976. This compound is used as a general purpose and high pressure lubricant and heat stabilizer for PVC compounds. Due to its many civilian uses, pollution from civilian uses of lead stearate is expected to be wide spread.

Lead stearate is moderately toxic to mammals. The toxicity of this compound to aquatic organisms is unknown. However due to its limited solubility, the aquatic toxicity should be low unless it is hydrolyzed to free lead.

Lead stearate is not a military unique chemical. Because of the limited use of this compound in propellant production, further studies by the Army should be of low priority.

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## FOREWORD

This report details the results of a preliminary problem definition study on lead stearate. The purpose of this study was to determine the Army's responsibility for conducting further research on lead stearate in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on lead stearate, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Lead stearate was only one of the 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

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## X. LEAD STEARATE

### A. Alternate Names

Lead stearate is a metallic soap used as a stabilizer for polyvinyl compounds. It exists in several forms depending on the conditions of manufacture. The pertinent alternate names for the various lead stearate compositions are given below:

#### Normal Lead Stearate

Molecular Formula:	$C_{18}H_{35}O_2 \cdot 1/2Pb$
Molecular Weight:	774.15 g/mole
CAS Registry No.:	1072-35-1
Replaces CAS Registry No's.:	5150-54-9; 11097-78-2; 15737-12-9; 37223-82-8
CA Name (9CI):	Octadecanoic acid, lead (2+) salt
CA Name (8CI):	Stearic acid, lead (2+) salt
Wiswesser Line Notation:	QV17 & 2Pb
Synonyms:	Lead distearate; Lead(II) stearate; Lead(2+) stearate; Normal lead stearate

#### Neutral Lead Stearate

Molecular Formula:	$C_{18}H_{35}O_2 \cdot xPb$
CAS Registry No.:	7428-48-0
Replaces CAS Registry No's.:	16893-63-3; 37223-94-2
CA Name (9CI):	Octadecanoic acid, lead salt
CA Name (8CI):	Stearic acid, lead salt
Wiswesser Line Notation:	QV17 & -Pb
Synonyms:	Austrostab 110E; Lead octadecanoate; Lead stearate; Listab 28; Neutral lead stearate

#### Dibasic Lead Stearate

Molecular Formula:	Unknown
CAS Registry No.:	52652-59-2
CA Name (9CI):	Octadecanoic acid, lead salt, dibasic
Synonyms:	Lead stearate, dibasic

### B. Physical Properties

The physical properties of the lead stearates are presented in Table X-1.

Table X-1. Physical Properties of Lead Stearate.\*

Normal Lead Stearate

Physical Form @ 20°C:	solid powder
Color:	white
Odor:	fatty
M.P.:	115.7°C
B.P.:	-
Refractive Index:	1.877, 1.822, 1.894
	soluble in toluene, turpentine, hot mineral oil
Specific Gravity:	1.34 g/cm <sup>3</sup>
Flash Point:	232°C
Solubility:	water - 0.005g/100g @ 35°C 0.006g/100g @ 50°C ethyl ether - 0.005g/100ml @ 14.5°C insoluble in alcohol

Dibasic Lead Stearate

Physical Form @ 20°C:	solid powder
Color:	white
M.P.:	decomposes
Specific Gravity:	2.00

\*References: Hodgman et al., 1963; Sax, 1975; Witco Chemical, 1978;  
Kirk and Othmer, 1965.

## C. Chemical Properties

### 1. General Reactions

Detailed investigations into the chemical behavior of lead stearate have not been reported in the literature. Lead stearate is slightly soluble in water (0.005 g/100g). Hydrolysis is expected to occur step-wise:



This hydrolysis and thus the solubility of lead stearate should increase as the pH decreases. In solutions of high pH, lead stearate would be expected to form soluble basic salts. These reactions will occur in the environment depending on the conditions encountered.

### 2. Sampling and Analysis

Quantitative analysis of organolead compounds may be accomplished by removing the organic constituent by oxidation. The resulting lead oxide may be determined by atomic absorption. Lead may also be determined colorimetrically with dithizone. The red lead dithizonate is quantitated by absorption at 520 nm (Franson, 1975).

## D. Uses in Army Munitions

### 1. Purposes

Lead stearate is used in conjunction with lead salicylate as burning rate modifiers in bermite grains. The amount of lead stearate in the formulation is 0.5%. Lead stearate is also used in the ROLAND propellant formulation. Propellants containing lead stearate are not in current Army production. However, they have been produced in the past at Radford AAP, Badger AAP and Sunflower AAP.

### 2. Quantities Used

#### a. Historical Use

Radford AAP procured 27,127 lb of lead stearate during the period 1968-1977. In 1972 and 1973, the purchase rates were 6,450 and 10,000 lb, respectively. Production statistics do not show any use of lead stearate in propellants during the period 1968-1977, however.

The specific amounts of this lead compound purchased by Radford AAP during 1968-1977 are listed below (Watts, 1978):

<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
1,500	5,100	2,250	0	6,450	10,000	0	844	733	250

b. Current Use

Lead stearate is not currently used in the manufacture of propellants at Radford AAP. Plans for future use of lead stearate are uncertain.

c. Use at Full Mobilization

The full mobilization use rate of lead stearate at Radford AAP would be approximately 300 lb/month for bermite grain and ROLAND propellant production.

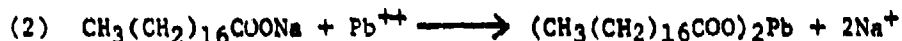
3. Documented or Speculated Occurrences in Air or Water

The actual concentration of lead stearate in waste streams has not been measured. Its use tends to be sporadic, therefore most of the time no lead stearate is being discharged. When lead stearate is in use, losses would be expected from chemical preparation operations and from solvent processing operations. This operation could lead to losses of 10 to 50 lb/month, ~50% of which would be expected to appear in the effluent streams which enter the New River.

E. Uses in the Civilian Community

1. Production Methodology

The manufacture of lead stearate consists of two chemical steps:



The reactions are run as batch processes. Stearic acid is added to an aqueous caustic soda solution to make a 5% sodium stearate solution. A 10-15% lead(II) salt solution is added slowly and lead stearate precipitates. The slurry is filtered, then washed. The crude lead stearate is dried and ground to uniform particles (Kirk and Othmer, 1965).

2. Manufacturers, Production and Capacity

The manufacturers of lead stearate are listed below:

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Table X-2. Manufacturers of Lead Stearate

Diamond Shamrock Corporation	Cedartown, Georgia
NL Industries Incorporated	Philadelphia, Pennsylvania
The Norac Company	Lodi, New Jersey
Smith Chemical and Color	Jamaica, New York
Witco Chemical Corporation	Clearing, Illinois

---

Diamond Shamrock, NI Industries, and the Norac Company also manufacture dibasic lead stearate (S.R.I., 1977). Individual plant capacities are unavailable. In 1976, U.S. production of lead stearate was 1,254,000 lb. Total metal stearate salt production was over 80 million pounds ( U.S. Tariff Commission, 1976).

### 3. Usages

Lead stearate is used as a general purpose and high pressure processing lubricant and medium-efficiency heat stabilizer for translucent and opaque PVC compounds (Witco Chemical, 1978). The stabilizing effect is due to its ability to accept hydrogen chloride. It is also used as a drier in paints and varnishes (Hawley, 1977).

### 4. Future Trends

Prior to 1976, U.S. production of lead stearate was too small to be reported separately from other metal stearates. Production is now greater than one million pounds per year. We are aware of no anticipated major changes in the civilian lead stearate market.

### 5. Documented or Speculated Occurrences in the Environment

There are no reports of lead stearate discharges into the environment from civilian production or uses.

### F. Comparison of Military and Civilian Uses and Pollution

In 1976, Radford AAP purchased 733 lb of lead stearate. This purchase represented only 0.06% of the lead stearate produced by the civilian community. At full mobilization, Radford AAP's use of lead stearate would reach 500 lb/month or 6000 lb/yr. If Sunflower and Badger AAPs also each used 6000 lb/yr at full mobilization, then the maximum military usage would be 18,000 lb/yr. This number represents only 1.4% of the 1976 civilian production.

The main pollution from lead stearate is due to the potential release of lead in the environment. Potential releases of as much as 1800 lb of lead stearate per year from Radford AAP, Badger AAP, and Sunflower AAP could occur at full mobilization. However, the quantity of lead entering the environment from lead stearate in propellant manufacture is insignificant compared to that entering the environment from other sources such as lead mining, refining, gasoline additives, etc.

### G. Toxicological and Environmental Hazards

#### 1. Toxicity to Mammals

The metallic stearates are widely used throughout the civilian

industry as stabilizers in polyvinyl chloride polymers. Although the lead stearate is used in relatively small amounts in the polyvinyl chloride polymers, many workers come in contact with it for long periods of time. Caille *et al.*, (1971) have reported cases of lead poisoning among factory workers engaged in the manufacture and use of lead stearate as well as those handling the products containing this compound.

In order to determine the potential hazards of the metal stearates to workers, Russian scientists have studied the acute and chronic effects of the metal stearates on rats. They administered monobasic and dibasic lead stearate to rats for several months by intratracheal instillation (Tarasenko *et al.*, 1976). The effects on lung tissue at various times and doses is presented in Table X-3. They found 46.6 of the animals died when given 50 mg of lead stearate intratracheally; 40% died when 25 mg of dibasic lead stearate was administered in the same manner. In these experiments, Tarasenko *et al.* (1976) observed the toxic effects of 5 mg of metal stearate administered by intratracheal instillation decrease in the order  $Cd > Ba > Ca > Zn > Pb$ . This ordering shows that the change in toxicity of the metals bound to stearic acid corresponds to their physical properties.

Tarasenko *et al.*, (1976) indicate that the metal stearates which they studied (including mono- and dibasic lead stearate) are absorbed through the skin. This statement is in direct contrast to claims by Witco Chemical Company. Witco claims that lead stearate is not absorbed through the skin. Further evaluation of the original Russian literature and of other toxicological studies on lead stearate is necessary to clarify this point.

## 2. Aquatic Toxicity

Soluble lead compounds can be highly toxic to organisms present in the aquatic environment. Normal levels of lead in natural water systems are less than 10 ppb (Ettinger, 1967). Typical values for total lead in fish are 0.5 ppm (Bowen, 1966). The available bioassay data indicate that a level of 100-200 ppb of lead can be toxic to fish (Lambou and Lim, 1970). Lead compounds were also shown to be much more toxic in soft water (less than 50 ppm  $CaCO_3$ ) than in hard water. This increase in toxicity is due to the availability of ionic lead to the organisms in soft water.

Only one study was retrieved from the literature which dealt specifically with the aquatic toxicity of lead stearate. Burton (1971) found no lethal effects when bluegills (*Lepomis macrochirus*) were exposed to 150 ppm of lead stearate. The water characteristics for this study were: pH 7.3-8.3 and hardness 35-51 ppm  $CaCO_3$ . Burton's data correlates with that of Lambou and Lim (1970) and Aronson (1971). In studies conducted by Lambou and Lim (1970), no toxic response was observed when fish were exposed to insoluble lead compounds. Carbonate and organic ligand lead compounds were also shown to have a low toxicity to fish (Aronson, 1971).

Table X-3. Effects of Intratracheal Instillation of Lead Stearates on Lung Tissues (Tarasenko *et al.*, 1976).

<u>Compound</u>	<u>Dose</u>	<u>Time</u>	<u>Observation</u>
Monobasic lead stearate	10	4 months	proliferation of adventitial cells; vasculitis
" "	50	2 months	lesions of blood vessel bed; in- creased vascular permeability; swelling and plasmorrhagia of the walls of small arteries
" "	50	6 months	marked sclerosis with foci of chronic alveolar emphysema
Dibasic lead stearate	5	4 months	mild peribronchial sclerosis
" "	25	2 months	peribronchial sclerosis; bronchial lesions
" "	25	8 months	foci of bronchiectases with peri- bronchial sclerosis; emphysema

Lead stearate is not used in propellant formulations currently being produced at Radford AAP. At full mobilization, Radford AAP would use ~500 lb/month of lead stearate. Effluents to the New River could be as high as 25 lb/month. However, other lead compounds are used in significantly larger quantities than the stearate, e.g., lead salicylate. Therefore, lead stearate losses do not have a significant impact on the lead levels in the New River.

### 3. Toxicity to Microorganisms

No specific microorganism toxicity data was found on lead stearate. However, lead concentrations of 1.0 ppm were found to be toxic to aerobic bacteria (McKee and Wolf, 1963). Microbial decomposition is inhibited by 0.1 to 0.5 ppm of lead.

### 4. Phytotoxicity

No phytotoxic information on lead stearate was encountered. However, phytotoxic data on lead was obtained and may be indirectly related.

The pattern of lead uptake by plants has been rarely studied and little can be concluded about the mechanism involved. The uptake of lead was reported constant with increasing levels of soil lead, until a certain point is reached when uptake becomes unrestricted and rises abruptly (Nicolls et al., 1965).

Only soluble lead salts and ionic lead are available to plant roots. The uptake of lead by ryegrass grown in a solution containing lead is shown in Table X-4 (Hepple, 1972). The total content of lead in roots plus shoots of perennial ryegrass increases with increasing levels in the soil. The roots take up lead readily but pass on only a small proportion to the shoots. Thus, the roots act as a barrier which restricts the movement of lead salt through the plant to growing animals. During winter months when plant growth is low, a considerable increase in the lead contents of the ryegrass shoots was observed. An 8-fold increase in total lead content of a soil did not cause any significant increase in the lead content of bromegrass grown on the soil in a greenhouse (Motto et al., 1970).

Corn was grown in the field where lead acetate had been soil-applied at eight rates ranging from 0 to 3,200 kg lead/ha. No changes in emergence, plant height, grain yield, color, maturity or other growth differences were observed during the 2-year study (Baumhardt and Welch, 1972).

Five crops (cauliflower, tomatoes, cabbage, strawberries and valencia oranges) were analysed for their lead content by Schuck and Locke (1970). These plants revealed little inclination to absorb lead via their root system (Schuck and Locke, 1970).



Table X-4. Lead Uptake by Perennial Ryegrass Grown  
in Solution-Culture (Hepple, 1972).

Level of Pb added to solution		Pb content of plants at 14 days after addition to solution			
		Roots		Shoots	
(ppm)	( $\mu$ g)	(ppm)	( $\mu$ g)	(ppm)	( $\mu$ g)
0.4*	400	98	201	3	37
1.0†	12500	3696	9610	104	1055

\* In 1 liter of static solution-culture; controlled environment experiment.

† In 12.5 liter of flowing solution-culture; glass-house experiment.

## H. Regulations and Standards

### 1. Air and Water Standards

There are no air and water standards specific for lead stearate. However criteria have been set for lead in potable and effluents (EPA, 1976). For potable water, the lead content can be no greater than 50 µg/l. Due to the variability of lead solubility and toxicity in different waters, the following criterion has been set for effluents (using the receiving water as a diluent).

- 0.01 times the 96-hour LC50 value expressed as dissolved lead for the most sensitive species.

This criterion requires that 96-hour LC50 test be performed with the actual water samples and the most sensitive species in the local ecosystem.

### 2. Human Exposure Standards

No specific standards for lead stearate have been set for occupational exposure to this chemical. However, a criteria document has recommended an air standard of 150 µg(Pb)/m<sup>3</sup> for lead stearate (NIOSH, 1977).

## I. Conclusions and Recommendations

In order to assess the Army's responsibility for conducting further work on lead stearate, the data presented in this report was gathered and evaluated. After evaluation of this data, the following conclusions were drawn:

- lead stearate is not a military unique chemical
- the civilian production is >1 million lb/year
- lead stearate is used for a variety of purposes in the civilian community which leads to widespread pollution
- the Army's use of this compound is sporadic and any future use is uncertain
- although lead stearate is toxic to mammals, it is probably relatively non-toxic to aquatic organisms; however, it could be bioaccumulated.

As a result of this preliminary problem definition study, it is concluded that toxicological and environmental evaluations of this compound are a civilian problem. Thus, further studies on this compound by the Army should be a low priority.

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AD

**PRELIMINARY PROBLEM DEFINITION STUDY OF  
48 MUNITIONS-RELATED CHEMICALS**

**VOLUME II PROPELLANT RELATED CHEMICALS**

**LEAD RESORCYLATE**

**FINAL REPORT**

**J. F. Kitchens  
W. E. Harward III  
D. M. Lauter  
R. S. Wentzel  
R. S. Valentine**

**April 1978**

**Supported by:**

**U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND  
Fort Detrick, Frederick, Maryland 21701**

**Contract No. DAMD17-77-C-7057**

**COTR: Clarence Wade, Ph.D.**

**ATLANTIC RESEARCH CORPORATION  
Alexandria, Virginia 22314**

**Approved for Public Release  
Distribution Unlimited**

**The findings in this report are not to be construed as an  
official Department of the Army position unless so design-  
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## SUMMARY

Lead resorcyate was developed in 1965 by NL Industries. Information on this compound is non-existent in the literature. There are no reported civilian uses of lead resorcyate. Thus it appears that the Army's propellant manufacture accounts for all civilian production of this compound.

Lead resorcyate is a military unique chemical. Further studies on this compound by the Army are recommended. These studies should include

- A Phase II detailed toxicological and environmental evaluation
- Determination of some of the physical and chemical properties of this compound if they can not be obtained from the manufacturer
- Sampling and analysis of sediment and biota at Radford AAP to determine the amount of accumulation
- Aquatic toxicity and bioaccumulation studies if the Phase II study indicates the need for this research
- Mammalian skin toxicity studies.

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## FOREWORD

This report details the results of a preliminary problem definition study on lead resorcyate. The purpose of this study was to determine the Army's responsibility for conducting further research on lead resorcyate in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on lead resorcyate, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Lead resorcyate was only one of the 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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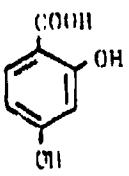
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## XI. LEAD RESORCYLATE

### A. Alternate Names

Lead resorcyate is a metallic soap formed from divalent lead and resorcylic acid, . The molecular formula of this compound is  $C_7H_5O_4 \cdot xPb$ .

Pertinent alternate names for lead resorcyate are listed below:

CAS Registry No.:	20936-32-7
CA Name (9CI):	Benzoic acid, 2,4-dihydroxy, lead salt
CA Name (8CI):	beta-resorcylic acid, lead salt
Synonyms:	Lead beta-resorcyate; Lead 2,4-dihydroxybenzoate

CAS Registry No.:	41453-51-4
Molecular Formula:	$C_7H_4O_4Pb$
CA Name (9CI):	Benzoic acid, 2,4-dihydroxy, lead(2+) salt(1:1)
Synonyms:	2,4-dihydroxybenzoatolead(II)

CAS Registry No.:	41453-50-3
Molecular Formula:	$C_7H_5O_4 \cdot 1/2 Pb$
CA Name (9CI):	Benzoic acid, 2,4-dihydroxy, lead(2+) salt (2:1)
Synonyms:	Bis(2,4-dihydroxybenzoate)lead(II)

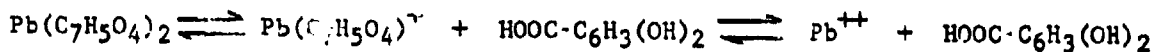
### B. Physical Properties

Lead resorcyate was first synthesized in 1965 by NL Industries. No literature on its physical properties is available.

### C. Chemical Properties

#### 1. General Reactions

Detailed investigations into the chemical behavior of lead resorcyate have not been reported in the literature. Lead resorcyate is slightly soluble in water. As with lead stearate and lead salicylate, step-wise hydrolysis is expected to occur



This hydrolysis and the solubility of lead resorcyate should increase as the pH decreases. In solution of high pH, lead resorcyate would be expected to form soluble basic salts. These reactions will occur in the environment depending on the conditions encountered.

## 2. Sampling and Analysis

Quantitative analysis of organolead compounds may be accomplished by removing the organic constituent by oxidation. The resulting lead oxide may be determined by atomic absorption. Lead may also be determined colorimetrically with dithizone. The red lead dithizonate is quantitated by absorption at 520 nm (Franson, 1975).

## 3. Uses in Army Munitions

### 1. Purposes

Lead resorcyate is used in the production of double base propellants made by both solvent and solventless processes. It is specified in the following formulations:

#### % lead resorcyate in formulation

ARP casting powder	3.0 ± 0.25
PNJ casting powder	2.93
PNJ for TOW	1.93
N-14	2.5
NOSIH-AA-2	0.5
NOSIH-AA-6	0.3
NOSIH-AM-2	2.5
N-12	2.0

Lead resorcyate has been used in the past by Badger AAP and Sunflower AAP. Current use in propellant formulations is limited to Radford AAP, however.

### 2. Quantities Used

#### a. Historical Use

Radford AAP has purchased an average of 45,000 lb/year of lead resorcyate over the period 1968-1977. Propellant production rates account for 7,060 lb/year of this amount, or about 16%. About 75% of the lead resorcyate in propellants was used for the PNJ and NOSIH-AA-6 formulations. The lead resorcyate which is not accounted for in propellants

(~84%) was sent to other facilities, or in some cases returned to the vendor. The specific amounts of this lead compound purchased by Radford AAP during 1968-1977 are listed below (Watts, 1978):

<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
189,300	149,521	398	692	14,355	30,934	24,034	12,620	23,537	5,266

b. Current Use

During 1977 an average of about 670 lb/month of lead resorcyate was used at Radford AAP. However, use of this chemical is sporadic. In December 1977, about 3000 lb were used in the production of 100,000 lb of ARP casting powder, or about 430% of the average rate.

c. Use at Full Mobilization

The full mobilization use rate of lead resorcyate at Radford is approximately 3000 lb/month.

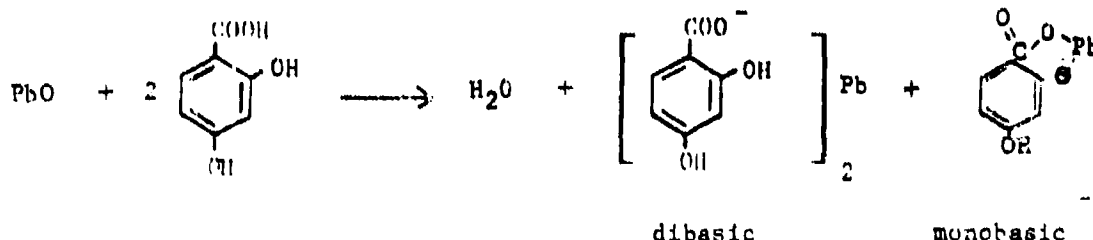
3. Documented or Speculated Occurrences in Air or Water

The actual concentration of lead resorcyate in waste streams from propellant manufacture has not been determined. The use of lead resorcyate tends to be sporadic, so, much of the time, none is being discharged. When lead resorcyate is in use, losses would be expected from chemical preparation operations and from solvent processing operations. This operation could lead to losses of 3-10% of the amount handled, or 90 to 300 lb/month at the December 1977 use rate. These amounts are also characteristic of full mobilization use rates. It is probable that ~1/2 of all the lead resorcyate lost will appear in effluent streams which ultimately reach the New River.

E. Uses in the Civilian Community

1. Production Methodology

Lead resorcyate is produced by the reaction of litharge (yellow) lead oxide) and resorcylic acid (NL Industries, 1978). The product is a mixture of the mono and dibasic salts:



The precipitate is filtered and the reaction medium recycled to reclaim dissolved material. The lead resorcyate is washed, then dried under dust collection. Figure XI-1 is a flow diagram of the process.

## 2. Manufacturers, Production, and Capacity

The manufacturers of lead resorcyate are listed below (S.R.I. 1977):

---

Table XI-1. Manufacturers of Lead Resorcyate.

Shepherd Chemical Co.	Cincinnati, OH
NL Industries	Oakland, CA; Philadelphia, PA

---

NL Industries also manufactures monobasic lead resorcyate (NL Industries, 1978).

Historical production figures, plant capacities, and details of the production process are unavailable due to their proprietary nature.

## 3. Usages

There are no reported civilian uses for lead resorcyate.

## 4. Future Trends

No civilian applications for lead resorcyate are anticipated.

## 5. Documented or Speculated Occurrences in the Environment

No environmental occurrences of lead resorcyate from the manufacturing processes have been reported.

## F. Comparison of Civilian and Military Uses and Pollution of Lead Resorcyate

Lead resorcyate is a metallic soap which is not used by the civilian community to any great extent. From the limited information obtained, the major and possibly the sole use of lead resorcyate is in propellants. The Army Ammunition plants (Radford, and Badger and Sunflower when operating) are the main polluters of this chemical. The pollution from lead resorcyate is minor compared to the total amount of lead entering the environment each year. However, this lead compound combined with lead stearate, lead salicylate and possibly other lead compounds could have a significant effect on the aquatic system at these Army Ammunition Plants.

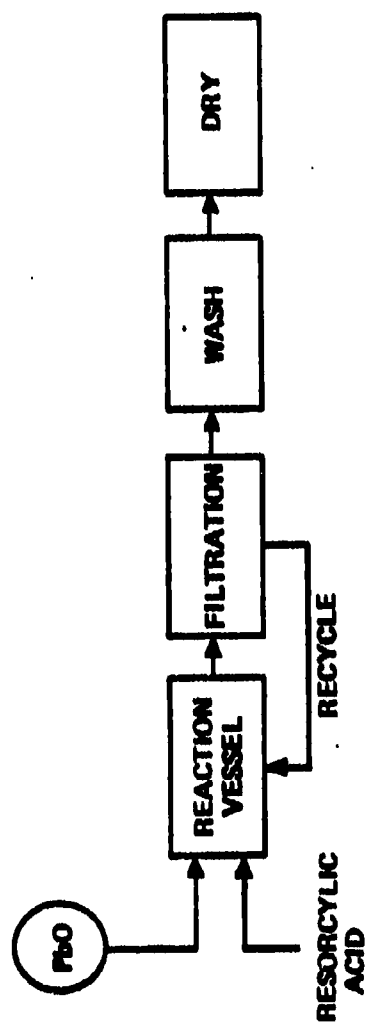


Figure XI-1. Manufacture of Lead Resorcyate.

## G. Toxicological and Environmental Hazards

### 1. Toxicity to Mammals

No data has been uncovered in the literature on the mammalian toxicity of lead resorcyate.

### 2. Aquatic Toxicity

No research has been conducted to determine the toxicity of lead resorcyate to aquatic organisms. Cairns and Dickson (1971) found the toxicity of a similar organo-lead compound to be low.

Lead resorcyate is probably degraded partially in the waste treatment effluent. However, the ability of microorganisms to degrade lead resorcyate has not been determined. The bioconcentration of lead is usually low, but organo-lead compounds could be accumulated in a similar manner as methyl-mercury.

At full mobilization, as much as 150 lb of lead resorcyate per month could enter the New River from Radford AAP. Due to the low solubility of lead resorcyate, most of this compound will be found in the sediment.

Weitzel *et al.* (1976) found lead levels in New River water between 1-2 ppb; lead levels in the sediment averaged over 100 ppm. From Weitzel's study, it is obvious that the sediment acts as a sink for lead. The long term effect of the accumulation of lead compounds in the sediment of New River could be an increased toxicity of the sediment to aquatic organisms.

### 3. Toxicity to Microorganisms and Invertebrates

No specific toxicity studies of lead resorcyate with microorganisms or invertebrates were reported in the literature.

### 4. Phytotoxicity

No phytotoxic information on lead resorcyate was encountered. However, phytotoxic data on lead was obtained and may be indirectly related.

The pattern of lead uptake by plants has been rarely studied and little can be concluded about the mechanism involved. The uptake of lead was reported constant with increasing levels of soil lead, until a certain point is reached when uptake becomes unrestricted and rises abruptly (Nicolle *et al.*, 1965).

Only soluble lead salts and ionic lead are available to plant roots. The uptake of lead by ryegrass grown in a solution containing lead



Table XI-2. Lead Uptake by Perennial Ryegrass Grown in Solution-Culture (Hepple, 1972).

Level of Pb added to solution		Pb content of plants at 14 days after addition to solution			
		Roots		Shoots	
(ppm)	( $\mu$ g)	(ppm)	( $\mu$ g)	(ppm)	( $\mu$ g)
0.4*	400	98	201	3	37
1.0†	12500	3696	9610	104	1055

\* In 1 liter of static solution-culture; controlled environment experiment.

† In 12.5 liter of flowing solution-culture; glass-house experiment.

is shown in Table XI-2 (Hopple, 1972). The total content of lead in roots plus shoots of perennial ryegrass increases with increasing levels in the soil. The roots take up lead readily but pass on only a small proportion to the shoots. Thus, the roots act as a barrier which restricts the movement of lead salt through the plant to growing animals. During winter months when plant growth is low, a considerable increase in the lead contents of the ryegrass shoots was observed. An 8-fold increase in total lead content of a soil did not cause any significant increase in the lead content of bromegrass grown on the soil in a greenhouse (Motto et al., 1970).

Corn was grown in the field where lead acetate had been soil-applied at eight rates ranging from 0 to 3,200 kg lead/ha. No changes in emergence, plant height, grain yield, color, maturity or other growth differences were observed during the 2-year study (Baumhardt and Welch, 1972).

Five crops (cauliflower, tomatoes, cabbage, strawberries and valencia oranges) were analyzed for their lead content by Schuck and Locke (1970). These plants revealed little inclinations to absorb lead via their root system (Schuck and Locke, 1970).

### 5. Availability of Literature for Phase II

No published U.S. literature on lead resorcyate was found. Data on this compound would have to come from the manufacturers files.

## H. Regulations and Standards

### 1. Air and Water Standards

There are no air and water standards specific for lead resorcyate. However criteria have been set for lead in potable and effluents (EPA, 1976). For potable water the lead content can be no greater than 50 µg/l. Due to the variability of lead solubility and toxicity in different waters, the following criterion has been set for effluents (using the receiving water as a diluent).

- 0.01 times the 96-hour LC50 value expressed as dissolved lead for the most sensitive species.

This criterion requires that 96-hour LC50 test be performed with the actual water samples and the most sensitive species in the local ecosystem.

### 2. Human Exposure Standards

No specific standards for lead resorcyate have been set for occupational exposure to this chemical. However, a criteria document has recommended an air standard of 150 µg(Pb)/m<sup>3</sup> for lead stearate (NIOSH, 1977). A similar TLV for lead resorcyate should afford workers adequate protection.

## I. Conclusions and Recommendations

Very little information was uncovered on lead resorcyate. This information lies in the files of the manufacturer. However, it appears that lead resorcyate is used solely by the Army in propellant manufacture. It is thus recommended that this compound be included in the Phase II study. Included in this effort should be a visit to the manufacturer and discussion with the personnel who worked on this compound. In addition, it is recommended that the following studies be initiated by the Army

- determination of some of the physical and chemical properties of this compound if they can not be obtained from the manufacturer.
- sampling and analysis of sediment and biota at Radford AAP to determine the amount of accumulation of lead resorcyate
- mammalian skin toxicity studies
- aquatic toxicity and bioaccumulation studies if the Phase II study indicates the need for this research.

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# List of Abbreviations

@	- at
AAP	- Army Ammunition Plant
avg	- average
BAAP	- Badger Army Ammunition Plant
BOD	- Biological Oxygen Demand
BOD5	- 5 day Biological Oxygen Demand
B.P.	- Boiling Point
Bu	- Butyl
°C	- Degrees Centigrade
CA	- Chemical Abstracts Service
CH <sub>2</sub> O	- Formaldehyde
8CI	- 8th Centennial Index
9CI	- 9th Centennial Index
cm <sup>-1</sup>	- Wave Number
CO <sub>2</sub>	- Carbon Dioxide
COC	- Cleveland Open Cup
COD	- Chemical Oxygen Demand
Cp	- Heat Capacity at Constant Pressure
d	- Density
DBP	- n-dibutyl Phthalate
DEHP	- Diethylhexyl Phthalate
Δ	- Heat
DEP	- n-diethyl Phthalate
DNT	- Dinitrotoluene
DOP	- Dioctyl Phthalate
E <sup>+</sup>	- Electrophile
EC50	- Concentration Required to Effect 50% of the Exposed Population
EPA	- Environmental Protection Agency
Et	- Ethyl
ETOH	- Ethanol
g	- Grams
GC	- Gas Chromatography
gpd	- Gallons per Day
H <sup>+</sup>	- Hydrogen Ion
H <sub>2</sub>	- Hydrogen
ha	- Hectare
HCl	- Hydrochloric Acid
HMX	- 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane
HNO <sub>2</sub>	- Nitrous Acid
HNO <sub>3</sub>	- Nitric Acid
H <sub>2</sub> O	- Water
H <sub>2</sub> SO <sub>4</sub>	- Sulfuric Acid
hν	- Light Energy
InAAP	- Indiana Army Ammunition Plant
IR	- Infrared
kg	- Kilogram
Kgpd	- Kilogallons per Day
LAAP	- Louisiana Army Ammunition Plant

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# List of Abbreviations (Continued)

LAP	- Load, Assembly and Pack
lb	- Pounds
LC50	- Concentration Required to Kill 50% of the Exposed Population
LD50	- Dose Required to Kill 50% of the Exposed Population
$\lambda_{max}$	- Wavelength of an Absorption Maxima
mgd	- Million Gallons per Day
mg/l	- Milligrams per Liter
mg/m <sup>3</sup>	- Milligrams per Cubic Meter
mo	- Month
M.P.	- Melting Point
mm	- Millimicron
NaCl	- Sodium Chloride
Na <sub>2</sub> CO <sub>3</sub>	- Sodium Carbonate
NaNO <sub>2</sub>	- Sodium Nitrite
NaOH	- Sodium Hydroxide
n <sub>D</sub>	- Refractive Index
ng	- Nanogram
ng/m <sup>3</sup>	- Nanograms per Cubic Meter
NH <sub>3</sub>	- Ammonia
NH <sub>4</sub> Cl	- Ammonium Chloride
nm	- Nanometer
No.	- Number
Pd	- Palladium
%	- Percent
pH	- Negative Log of the Hydrogen Ion Concentration
ppb	- Parts per Billion
ppm	- Parts per Million
Pt	- Platinum
R	- Alkyl Group
ROH	- Aliphatic Alcohol
SAAP	- Sunflower Army Ammunition Plant
SbCl <sub>5</sub>	- Antimony Pentachloride
TC	- Total Carbon
TDLo	- Lowest Dose for Which an Effect was Observed in the Exposed Population
TLV	- Threshold Limit Value
TOC	- Total Organic Carbon
TSS	- Total Suspended Solid
vol	- Volume
ZnCl <sub>2</sub>	- Zinc Chloride

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